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Anthracene-Bridged Binuclear Ruthenium Complexes: Electrochemical and Spectroscopic Evidence of Electronic Communication Through the π System

Neus Vilà, Yu-Wu Zhong, Jay C. Henderson, and Héctor D. Abruña*

Baker Laboratory, Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853-1301

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Six dinuclear cyclometalated ruthenium complexes, **1**−**6**, based on diphenylanthracene (DPA) and anthracene (AN) as bridging ligands have been synthesized and fully characterized electrochemically and spectroscopically. The anodic electrochemistry of the homobinuclear ruthenium complexes, **1**−**6**, has been examined in three different nonaqueous solvents (ACN, DMF, and CH_2Cl_2). The ability of the anthracene derivatives to transmit electronic effects between the two redox units has been demonstrated by the observed splitting of the voltammetric signals ascribed to the metal centers. The electronic communication has also been evidenced by the presence of intervalence charge transfer transition bands in the near-infrared region of the spectrum due to an intramolecular electron transfer process mediated by the bridge when the mixed valence species (Ru^{II}/Ru^{III}) are electrochemically generated. Cyclic voltammetric measurements have been carried out under different conditions of solvent and supporting electrolyte. Differences in $\Delta E^{\circ\prime}$, the potential separation of the formal potentials of the metal-based anodic processes, have been observed and found to depend on the medium employed. These differences have been ascribed to different degrees of ion pairing. Such effects can be, in turn, modulated as a function of not only the polarity and donor strength of the solvent but also of the coordinating capacity of the anion employed as a supporting electrolyte.

Introduction

Long-range communication, including electron and energy transfer between remote metal centers in multimetallic assemblies, is one of the most fundamental aspects of information conveying in molecular systems and of great potential use in molecular electronics. Mixed-valence compounds, particularly species containing metallic centers in different oxidation states, have been widely employed to study intramolecular electron transfer (ET) processes between donor and acceptor sites. Robin and Day[1] classified mixed-valence systems, including molecules, metal complexes, and solid-state materials, as a function of the strength of the electronic interaction (coupling) between donor and acceptor sites. Such classification takes into account three situations for valence exchange. In this sense, species included in class I essentially display zero metal−metal interaction. Class II includes species for which a nonzero barrier for valence exchange might exist. The sensitivity of mixed-valence metal complexes toward the medium (solvent/electrolyte),[2−24] an experimental factor which has been carefully discussed in previous reports by several authors, has been demonstrated in a number of systems. Furthermore, although the comproportionation constant, K_c, determined from electrochemical data, is indicative of the strength of the metal−metal

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*To whom correspondence should be addressed. E-mail: hda1@cornell.edu.

(1) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.
(2) Barbara, P. F.; Meyer, T. J.; Ratner, M. A. *J. Phys. Chem.* **1996**, *100*, 13148.
(3) Chen, P.; Meyer, T. J. *Chem. Rev.* **1998**, *98*, 1439.
(4) Nelsen, S. F. *Chem.—Eur. J.* **2000**, *6*, 581.
(5) Demadis, K. D.; Hartshom, C. M.; Meyer, T. J. *Chem. Rev.* **2001**, *101*, 2655.
(6) Keene, F. R. *Coord. Chem. Rev.* **1997**, *166*, 121.
(7) Keene, F. R. *Chem. Soc. Rev.* **1998**, *27*, 185.
(8) D'Alessandro, D. M.; Keene, F. R. *Chem. Soc. Rev.* **2006**, *35*, 424.
(9) Kaim, K.; Kasack, V. *Inorg. Chem.* **1990**, *29*, 4696.
(10) Heilmann, M.; Frantz, S.; Kim, W.; Fiedler, J.; Duboc, C. *Inorg. Chim. Acta* **2006**, *359*, 821.
(11) Barrière, F.; Camire, N.; Geiger, W. E.; Mueller-Westerhoff, U. T.; Sanders, R. *J. Am. Chem. Soc.* **2002**, *124*, 7262.
(12) D'Alessandro, D. M.; Keene, F. R. *Dalton Trans.* **2004**, 3950.
(13) LeSuer, R. J.; Geiger, W. E. *Angew. Chem., Int. Ed.* **2000**, *39*, 248.
(14) Juhasz, M.; Hoffmann, S.; Stoyanov, E.; Kim, K.-C.; Reed, C. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 5352.
(15) Reed, C. A. *Chem. Commun.* **2005**, 1669.
(16) Xie, Z.; Jelinek, T.; Bau, R.; Red, C. A. *J. Am. Chem. Soc.* **1994**, *116*, 1907.
(17) Kaim, W.; Lahiri, G. K. *Angew. Chem., Int. Ed.* **2007**, *46*, 1778.
(18) D'Alessandro, D. M.; Keene, F. R. *Chem. Phys.* **2006**, *324*, 8.
(19) D'Alessandro, D. M.; Junk, P. C.; Keene, F. R. *Supramol. Chem.* **2005**, *17*, 529.
(20) D'Alessandro, D. M.; Topley, A. C.; Davies, M. S.; Keene, F. R. *Chem.—Eur. J.* **2006**, *12*, 4873.
(21) Fellows, E. A.; Keene, F. R. *J. Phys. Chem. B* **2007**, *111*, 6667.
(22) DeRosa, M. C.; White, C. A.; Evans, C. E. B.; Crutchley, R. J. *J. Am. Chem. Soc.* **2001**, *123*(7), 1396.
(23) Reimers, J. R.; Hush, N. S. *J. Chem. Phys.* **2005**, *319*, 39.
(24) D'Alessandro, D. M.; Keene, F. R. *Pure Appl. Chem.* **2008**, *80*, 1.

interaction in a way similar to the electronic interaction energy and intensity of the intervalence charge transfer (IVCT), some reports have demonstrated that these two manifestations of metal−metal interactions can differ in magnitude depending on the nature of the bridging ligands.[3−5,18−39] Mixed-valence species categorized as class III are based on electron delocalized systems with possibly fractional oxidation states. Electron transfer between redox sites occurs in the absence of an activation barrier. A new class of species, class II−III or a borderline situation, was introduced in 1998 by Meyer and Chen[3] to address the behavior of mixed-valence ruthenium and osmium complexes.

It has been previously well-documented that mixed-valence metal complexes, bridged by conjugated organic ligands and capped with redox-active organometallic termini, allow facile intramolecular electron transfer to occur along the molecular backbone. The study of ET through mixed-valence compounds is a very active field of research. A large number of compounds have been synthesized, allowing for the study of various factors such as the distance between the redox centers, solvent effects, and the nature of the bridging ligand.[1,40−46] Linear organometallic compounds with extended π-conjugated backbones are attractive potential candidates as molecular wires that might operate as connectors allowing electron flow to occur between different elements of nanoscale electronic devices by virtue of the possible charge delocalization along the conjugated molecular backbone. Electrochemical measurements and spectroscopic studies in the near-infrared region are often employed to evaluate the extent of electronic communication between remote electroactive organometallic groups and to gain insight into metal-to-metal charge transfer processes in mixed-valence species with extended π delocalization. Important contributions to this issue have been provided by Keene, reporting differences in the physical properties of diastereoisomers of several dinuclear complexes,[6,7] which could explain some particular solvent effects on the IVCT bands observed.[18,45] Keene has also focused on different factors such as structural influences or the effect of anions on the IVCT bands, providing new insights into crucial factors that can affect intermetal communication.

Cyclometalated transition metal complexes have found widespread interest as species with promising properties in various fields owing to the strong σ-donating ability of the cyclometalating ligand. Some examples of binuclear ruthenium and osmium complexes linked by cyclometalating ligands[47,48] have been previously reported and compared to the analogous species built with bis(terpyridine)-type ligands.[28,29] In most of the species investigated, metal−metal couplings were found to be much stronger for the cyclometalated derivatives, and this has been ascribed to better overlap of the molecular orbitals for these complexes. Typically, the coordinating ligand forms a bond to the metal center, and then, intramolecular C−H activation takes place to yield a five-membered chelate ring.[47−49]

It is well-known that $E^{\circ\prime}$ shifts are sensitive to both solvent and supporting electrolyte effects,[50−54] and there have been recent systematic studies illustrating that the effects of changes in the supporting electrolyte anion on the $\Delta E^{\circ\prime}$ values of oxidations involving cationic products can be large.[3,12,55,56]

In this manuscript, we report on the spectral and electrochemical characterization of six binuclear ruthenium complexes based on anthracene derivatives as bridging ligands (see Chart 1). The influence of the medium on the comproportionation constants determined from electrochemical data is demonstrated, suggesting that the metal-to-metal distance and the possibility of direct d−d overlap in the case of small bridging ligands are not the only factors contributing to the magnitude of K_c in binuclear complexes, as recently pointed out by other authors. Our particular interest in these compounds arises from their potential application as materials for molecular electronics and data storage.

Experimental Section

Characterization and Instrumentation. General. All reactions were carried out under an inert atmosphere of nitrogen using standard Schlenk techniques unless otherwise noted. ^{1}H

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(25) Poppe, J.; Moscherosh, M.; Kaim, W. *Inorg. Chem.* **1993**, *32*, 2640.

(26) Chanda, N.; Sarkar, B.; Fiedler, J.; Kaim, W.; Lahiri, G. K. *Inorg. Chem.* **2004**, *43*, 5128.

(27) Ghuman, S.; Sarkar, B.; Chanda, N.; Sieger, M.; Fiedler, J.; Kaim, W.; Lahiri, G. K. *Inorg. Chem.* **2006**, *45*, 7955.

(28) Collin, J.-P.; Lainé, P.; Launay, J.-P.; Sauvage, J.-P.; Sour, A. *J. Chem. Soc. Chem. Comm.* **1993**, 434.

(29) Beley, M.; Collin, J.-P.; Louis, R.; Metz, B.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1991**, *113*, 8521.

(30) Knödler, A.; Fiedler, J.; Kaim, W. *Polyhedron* **2004**, *23*, 701.

(31) Marin, T. W.; Homoelle, B. J.; Spears, K. G.; Hupp, J. T.; Spreer, L. O. *J. Phys. Chem. A* **2002**, *106*, 1131.

(32) Patoux, C.; Launay, J.-P.; Beley, M.; Chodorowski-Kimmes, S.; Collin, J.-P.; James, S.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1998**, *120*, 3717.

(33) Beley, M.; Chodorowski-Kimmes, S.; Collin, J.-P.; Lainé, J.-P.; Launay, J.-P.; James, S.; Sauvage, J.-P. *Angew. Chem., Int. Ed.* **1994**, *33*, 1775.

(34) Sutter, J.-P.; Grove, D. M.; Beley, M.; Collin, J.-P.; Veldman, N.; Spek, A. L.; Sauvage, J.-P.; Van Koten, G. *Angew. Chem., Int. Ed.* **1994**, *33*, 1282.

(35) Kaim, W.; Klein, A.; Glöckle, M. *Acc. Chem. Res.* **2000**, *33*, 755.

(36) Kaim, W.; Sarkar, B. *Coord. Chem. Rev.* **2007**, *251*, 584.

(37) Fox, M. A.; Farmer, J. D.; Roberts, R. L.; Humphrey, M. G.; Low, P. J. *Organometallics* **2009**, *28*, 5266.

(38) (a) Gagliardo, M.; Amijs, C. H. M.; Lutz, M.; Spek, A. L.; Havenith, R. W. A.; Hartl, F.; van Klink, G. P. M.; van Koten, G. *Inorg. Chem.* **2007**, *46*, 11133. (b) Ward, M. D.; McCleverty, J. *J. Chem. Soc., Dalton Trans.* **2002**, 275 and references cited therein.

(39) Richardson, C.; Fitchett, C. M.; Keene, F. R.; Steel, P. J. *Dalton Trans.* **2008**, 2534.

(40) Brunschwig, B. S.; Creutz, C.; Sutin, N. *Chem. Soc. Rev.* **2002**, *31*, 168.

(41) Nelsen, S. F. *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: Weinheim, Germany, 2001; Vol. *1*, Chapter 10.

(42) Launay, J.-P.; Coudret, C. *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: Weinheim, Germany 2001; Vol. *5*, Chapter 1.

(43) D'Alessandro, D. M.; Kelso, L. S.; Keene, F. R. *Inorg. Chem.* **2001**, *40*, 6841.

(44) D'Alessandro, D. M.; Keene, F. R.; Steel, P. J.; Sumby, C. J. *Aust. J. Chem.* **2003**, *56*, 657.

(45) D'Alessandro, D. M.; Keene, F. R.; Bergman, S. D.; Kol, M. *Dalton Trans.* **2005**, 332.

(46) Slater, J. W.; D'Alessandro, D. M.; Keene, F. R.; Steel, P. J. *Dalton Trans.* **2006**, 1954.

(47) Lees, A. *J. Chem. Rev.* **1987**, *87*, 711.

(48) Chodorowski-Kimmes, S.; Beley, M.; Collin, J. P.; Sauvage, J. P. *Tetrahedron Lett.* **1996**, *37*, 2963.

(49) Barigelletti, I.; Ventura, B.; Collin, J. P.; Kayhanian, R.; Gavina, P.; Sauvage, J. P. *Eur. J. Inorg. Chem.* **2000**, *113*, 119.

(50) Evans, D. H.; Lehmann, M. W. *Acta Chem. Scand.* **1999**, *53*, 765.

(51) Barthel, J.; Gores, H.-J.; Schmeer, G.; Wachter, R. *Top. Curr. Chem.* **1983**, *111*, 33.

(52) Sawyer, D. T.; Sobkowiak, A.; Roberts, J. *Electrochemistry for Chemists*, 2nd ed.; John Wiley & Sons: New York, 1995, Chapter 7.

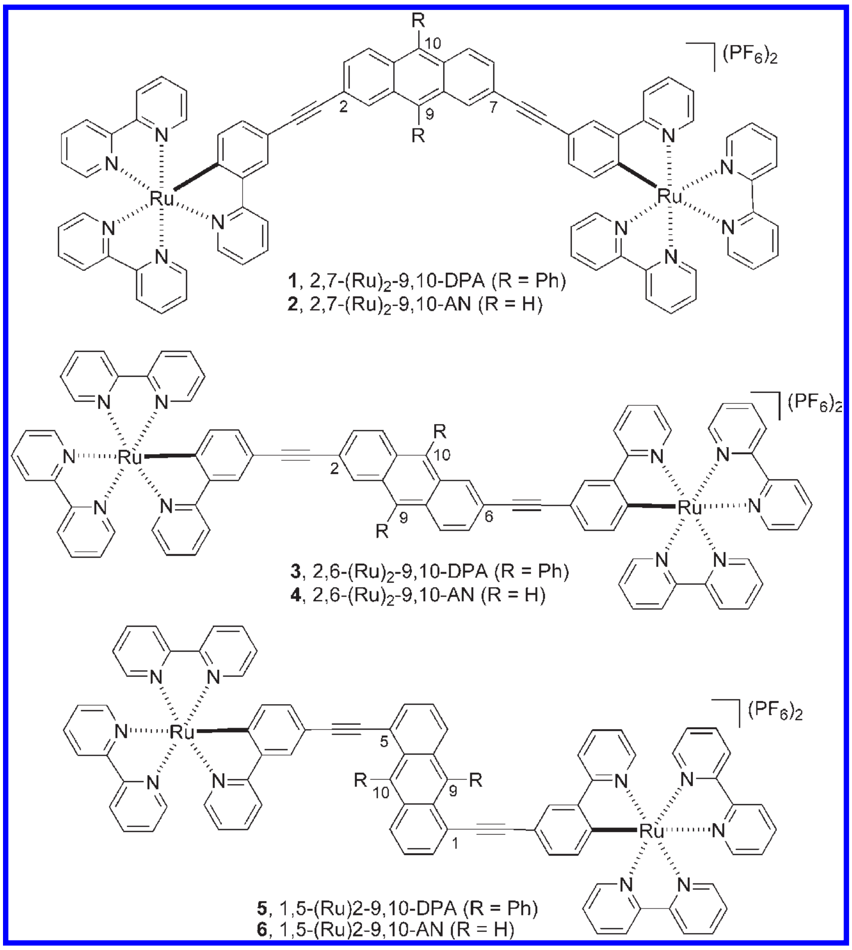
(53) Barriére, F.; Geiger, W. E. *J. Am. Chem. Soc.* **2006**, *128*, 3980.

(54) Chong, D.; Slote, J.; Geiger, W. E. *J. Electroanal. Chem.* **2009**, *630*, 28.

(55) (a) Yang, J.; As, A.; Rawashdeh, A.-M. M.; Sotiriou-Leventis, C.; Panzner, M. J.; Tyson, D. S.; Kinder, J. D.; Leventis, N. *Chem. Mater.* **2004**, *16*, 3457–3468. (b) Yang, W. J.; Kim, D. Y.; Jeong, M.-Y.; Kim, H. M.; Lee, Y. K.; Jeon, S.-J.; Cho, B. R. *Chem.—Eur. J.* **2005**, *11*, 4191.

(56) Ren, T. *Chem. Rev.* **2008**, *108*, 4185.

Chart 1. Binuclear Complexes **1**−**6**



NMR (300 MHz) spectra were recorded on a Varian Mercury 300 MHz FT-NMR spectrometer and referenced relative to residual proton resonances.

Instrumentation. Cyclic voltammograms were performed using either a BAS Epsilon potentiostat or a PAR 273A potentiostat. Three-compartment electrochemical cells were employed, and all measurements were carried out at room temperature under a nitrogen atmosphere. A glassy carbon electrode (3 mm diameter) was employed as a working electrode and a platinum wire as a counter electrode. All potentials are referenced to a Ag/AgCl reference electrode.

UV/vis/NIR spectra were performed on a Shimazdu UV-3101PC spectrophotometer.

Materials. All solvents and chemicals for synthesis were commercially available, of reagent-grade quality, and used without any further purification, except as noted below.

Experiments involving air- or water-sensitive reagents were carried out using standard Schlenck line techniques under a nitrogen atmosphere.

2,6-Diamino-anthraquinone (97%+), anthrone (97%+), copper(II) bromide (99%+), tetra-*n*-butyl ammonium hexafluorophosphate (n-Bu$_4$NPF$_6$; 98%), and tetra-*n*-butyl-ammonium chloride (n-Bu$_4$NCl) were purchased from Aldrich Chemical Co. and used as received. Tetra-*n*-butyl-ammonium tetrakis(pentafluorophenyl)borate (n-Bu$_4$NB(C$_6$F$_5$)$_4$) was prepared as described by Geiger and co-workers.[53,54] 1,5-Diamino-anthraquinone (85%+) was from Aldrich Chemical Co.

2,7-Dinitro-9,10-anthraquinone, 2,7-diamino-9,10-anthraquinone, 2,7-dibromo-9,10-anthraquinone, 2,6-dibromo-9,10-anthraquinone, 1,5-dibromo-9,10-anthraquinone, 2,6-dibromo-9,10-diphenylanthracene, 2,7-dibromo-9,10-diphenylanthracene, 1,5-dibromo-9,10-diphenylanthracene, 2,6-dibromo-9,10-anthracene, 2,7-dibromo-9,10-anthracene, and 1,5-dibromo-9,10-anthracene were prepared following literature procedures.[55−59]

The preparation of the binuclear ruthenium complexes, **1**−**6**, consisted of the separate synthesis of the anthracene and diphenylanthracene precursors and the mononuclear complex, [Ru(bpy)$_2$(Br-phpy)](PF$_6$), as described below.

Synthesis of 2,7-Bis(ethynyl)-9,10-diphenylanthracene. 2,7-Dibromo-9,10-diphenylanthracene was converted into 2,7-bis(trimethylsilyl)-9,10-diphenylanthracene by following a literature procedure.[55−59] 2,7-Bis(ethynyl)-9,10-diphenylanthracene was synthesized from 2,7-dibromo-9,10-anthraquinone, which was obtained via Sandmeyer reaction from the corresponding 2,7-diamino-9,10-anthraquinone afforded by following a procedure described in the literature.[60] To prepare 2,7-bis(ethynyl)-9,10-diphenylanthracene derivatives, dibromo-9,10-anthraquinones were first reacted with phenyl magnesium bromide in anhydrous tetrahydrofuran at room temperature and subsequently treated with Zn powder in aqueous acetic acid solution at 120 °C. On the other hand, to afford the simplest anthracene cores, 9,10-anthraquinones were reduced with sodium borohydride, yielding 9,10-dihydroxy-9,10-dihydroanthracenes in methanol that were subsequently converted to the

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(57) Criswell, T. R; Klanderman, B. H. *J. Org. Chem.* **1974**, *39*, 770.

(58) Lu, Z.; Lord, S. J.; Wang, H.; Moerner, W. E.; Twieg, R. J. *J. Org. Chem.* **2006**, *71*, 9651.

(59) Hodge, P.; Power, G. A.; Rabjohs, M. A. *Chem. Commun.* **1997**, 73–74.

(60) Villegas, J. M.; Stoyanov, S. R.; Huang, W.; Lockyear, L. L.; Reibenspies, J. H.; Rillema, P. *Inorg. Chem.* **2004**, 6383.

corresponding anthrones by dehydratation in aqueous hydrochloric acid. Reduction of the anthrones was performed by reaction with sodium borohydride, yielding the dibromo substituted anthracenes. A Sonogashira coupling reaction between 2,7-dibromo-9,10-diphenylanthracene and ethynyltrimethylsilane followed by deprotection of the trimethylsilyl groups by refluxing the mixture for 12 h in the presence of 2 equiv of potassium fluoride in methanol afforded the 2,7-bis(ethynyl)-9,10-diphenylanthracene derivative. In turn, 2,6- and 1,5-bis(ethynyl)-9,10-diphenylanthracene derivatives were synthesized by following the same methodology from 2,6- and 1,5-diamino-9,10-anthraquinones, which were from commercial sources.

2,7-Bis(ethynyl)-9,10-diphenylanthracene. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.65 (d, 2 H), 7.54 (d, 2 H), 7.45 (dd, 2 H), 7.38 (ddd, 4 H), 7.15 (m, 6 H), 2.95 (s, 2 H).

2,6-Bis(ethynyl)-9,10-diphenylanthracene. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.63 (d, 2 H), 7.56 (d, 2 H), 7.53 (dd, 2 H), 7.38 (dd, 4 H), 7.17 (m, 6 H), 2.78 (s, 2 H).

1,5-Bis(ethynyl)-9,10-diphenylanthracene. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.75 (d, 2 H), 7.45 (m, 6 H), 7.30 (m, 8 H), 2.88 (s, 2 H).

Synthesis of 2,7-Bis(ethynyl)anthracene. To obtain 2,7-Bis(ethynyl)anthracene, 2,7-dibromo-9,10-anthraquinone was first reduced with sodium borohydride, yielding 2,7-dibromo-9,10-dihydroxy-9,10-dihydroanthracene in methanol that was converted to the corresponding anthrones by dehydratation in aqueous hydrochloric acid. Reduction of the anthrone was performed by reaction with sodium borohydride, yielding the dibromo substituted anthracene. A similar procedure was employed to obtain the 2,6- and 1,5-Bis(ethynyl) derivatives from the appropriate precursors.

2,7-Bis(ethynyl)anthracene: 80% yield from 2,7-dibromoanthracene. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.52 (s, 1 H), 8.37 (s, 1 H), 8.23 (d, J = 8.43 Hz, 2 H), 8.05 (d, J = 1.97 Hz, 2 H), 7.47 (dd, J = 8.43 Hz, J = 1.97 Hz, 2 H), 2.98 (s, 2 H).

2,6-Bis(ethynyl)anthracene: 82% yield from 2,6-dibromoanthracene. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.45 (s, 2 H), 8.15 (d, J = 8.23 Hz, 2 H), 7.99 (d, J = 1.85 Hz, 2 H), 7.77 (dd, J = 8.23 Hz, J = 1.85 Hz, 2 H), 3.08 (s, 2 H).

1,5-Bis(ethynyl)anthracene: 77% yield from 1,5-dibromoanthracene. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.89 (s, 2 H), 8.10 (m, 2 H), 7.67 (m, 4 H), 2.88 (s, 2 H).

Preparation of the Mononuclear Brominated Ruthenium Complex, [Ru(bipy)$_2$(*p*-Brphpy)]PF$_6$. The preparation of the monometallic ruthenium complex was performed from commercial ruthenium trichloride following a synthetic procedure described in the literature.[60−63] *cis*-[Ru(bipy)$_2$Cl$_2$] was first prepared by refluxing a mixture of ruthenium trichloride and bipyridine in the presence of LiCl in dimethylformamide overnight.[60,61] Subsequently, reaction with an excess of 2-phenylpyridine in the presence of silver(I) tetrafluoroborate afforded [Ru(bipy)$_2$(phpy)](BF$_4$).[62] An exchange reaction was carried out in a methanolic solution containing NH$_4$PF$_6$ that afforded [Ru(bipy)$_2$(phpy)](PF$_6$) as a red dark crystalline solid. The singly brominated compound, [Ru(bipy)$_2$(*p*-Brphpy)]PF$_6$, was obtained upon treatment of the complex with 1.1 equiv of *N*-bromosuccinimide in acetonitrile at room temperature, as previously reported.[63]

Palladium-Catalyzed Cross Coupling Reaction for the Synthesis of the Homobimetallic Compounds (1−6). The homobinuclear complexes, **1**−**6**, were afforded following a procedure slightly modified from the literature for similar binuclear complexes.[64] A solution of the monobrominated mononuclear ruthenium complex (150 mg, 0.19 mmol), Pd(PPh$_3$)$_4$ (10 mg, 0.01 mmol), CuI (10 mg, 0.05 mmol), triethylamine (1 mL), and 0.09 mmol of the bis(ethynyl)-9,10-anthracene derivative in 5 mL of DMF were heated under argon for 48 h. Afterward, the solvent was removed in vacuo. To the red residue was added NH$_4$PF$_6$ (100 mg) in acetonitrile (5 mL). The solution was stirred and evaporated to dryness. The complex was dissolved in CH$_2$Cl$_2$, while the excess PF$_6^-$ salt remained undissolved. After filtration, the solvent was removed, and the resulting dark red solid was purified by column chromatography on silica gel with 4:6 toluene/acetonitrile as the mobile phase. The complex was completely desorbed in a concentrated NH$_4$PF$_6$ solution in acetonitrile. After removal of the solvent, the residue was redissolved in CH$_2$Cl$_2$, and then the solution was concentrated and diethyl ether was added to precipitate the complex.

Complex 1. A 25% yield from 2,7-bis(ethynyl)-9,10-diphenylanthracene was acheived. ^{1}H NMR (300 MHz, d_6-DMSO): δ 8.58−8.76 (m, 8 H), 8.05−8.15 (m, 6 H), 7.85−7.97 (m, 10 H), 7.42−7.77 (m, 16 H), 7.23−7.36 (m, 8 H), 6.94−7.13 (m, 6 H), 6.74−6.90 (m, 6 H), 6.30 (d, J = 8.02 Hz, 2 H). ^{13}C NMR (75 MHz, d_6-DMSO) δ: 175.4, 158.1, 152.3, 149.5, 148.7, 146.9, 140.2, 138.0, 136.5, 134.3, 133.1, 132.4, 129.8, 129.0, 127.8, 127.3, 124.9, 122.3, 121.6, 115.3, 101.2, 98.79. ES-MS *m*/*z*: 1654.9 (M − PF$_6$)$^+$, 1242.4 (M − PF$_6$ − Ru(bpy)$_2$)$^+$, 755.1 (M − 2PF$_6$)$^{2+}$. Anal. Calcd for $C_{92}H_{62}F_{12}N_{10}P_2Ru_2$: C, 61.40; H, 3.45; N, 7.79. Found: C, 61.62; H, 3.63; N, 7.91.

Complex 2. A 21% yield from 2,7-bis(ethynyl)anthracene was achieved. ^{1}H NMR (300 MHz, d_6-DMSO): δ 6.32 (d, J = 8.45 Hz, 2 H), 6.75−6.85 (m, 6 H), 7.01−7.05 (m, 6 H), 7.36−7.78 (m, 8 H), 7.84−7.92 (m, 14 H), 7.94−8.15 (m, 10 H), 8.58−8.76 (m, 8 H). ^{13}C NMR (75 MHz, d_6-DMSO): δ 176.3, 157.5, 153.3, 149.7, 148.9, 147.3, 139.2, 137.3, 136.5, 134.3, 133.9, 132.1, 130.1, 129.5, 129.0, 124.2, 121.6, 120.8, 118.9, 100.9, 98.99. ES-MS *m*/*z*: 1502.2 [M − (PF$_6$)]$^+$, 1090.3 [M − PF$_6$ − Ru(bpy)$_2$]$^+$, 678.9 [M − 2PF$_6$]$^{2+}$. Anal. Calcd for $C_{80}H_{54}F_{12}N_{10}P_2Ru_2$: C, 58.33; H, 3.28; N, 8.51. Found: C, 58.22; H, 3.48; N, 8.41.

Complex 3. A 22% yield from 2,6-bis(ethynyl)-9,10-diphenylanthracene was achieved. ^{1}H NMR (300 MHz, d_6-DMSO): δ 8.45−8.76 (m, 8 H), 8.15−8.37 (m, 6 H), 7.85−8.04 (m, 10 H), 7.40−7.73 (m, 16 H), 7.25−7.36 (m, 8 H), 6.74−7.03 (m, 6 H), 6.44−6.70 (m, 6 H), 6.30 (d, J = 8.02 Hz, 2 H). ^{13}C NMR (75 MHz, d_6-DMSO): δ 173.6, 157.6, 151.1, 149.7, 148.1, 146.9, 141.2, 137.5, 137.1, 135.9, 134.1, 133.4, 130.8, 129.0, 128.8, 127.9, 125.9, 123.1, 122.6, 114.7, 100.2, 97.9. ES-MS *m*/*z*: 1654.3 (M − PF$_6$)$^+$, 1241.9 (M − PF$_6$ − Ru(bpy)$_2$)$^+$, 755.5 (M − 2PF$_6$)$^{2+}$. Anal. Calcd for $C_{92}H_{62}F_{12}N_{10}P_2Ru_2$: C, 61.40; H, 3.45; N, 7.79. Found: C, 61.572; H, 3.45; N, 8.05.

Complex 4. A 27% yield from 2,6-bis(ethynyl)anthracene was achieved. ^{1}H NMR (300 MHz, d_6-DMSO): δ 6.28 (d, J = 8.15 Hz, 2 H), 6.75−6.95 (m, 6 H), 7.11−7.25 (m, 6 H), 7.28−7.65 (m, 8 H), 7.72−7.85 (m, 14 H), 7.99−8.35 (m, 10 H), 8.58−8.76 (m, 8 H). ^{13}C NMR (75 MHz, d_6-DMSO): δ 177.2, 156.4, 152.8, 147.7, 146.9, 142.9, 138.9, 136.2, 134.5, 134.3, 132.9, 132.0, 131.1, 130.5, 129.6, 126.2, 122.6, 121.8, 113.7, 100.1, 97.6. ES-MS *m*/*z*: 1502.7 [M − (PF$_6$)]$^+$, 1089.9 [M − PF$_6$ − Ru(bpy)$_2$]$^+$, 678.6 [M − 2PF$_6$]$^{2+}$. Anal. Calcd for $C_{80}H_{54}F_{12}N_{10}P_2Ru_2$: C, 58.33; H, 3.28; N, 8.51. Found: C, 58.29; H, 3.37; N, 8.75.

Complex 5. A 17% yield from 1,5-bis(ethynyl)-9,10-diphenylanthracene was achieved. ^{1}H NMR (300 MHz, d_6-DMSO): δ 8.45−8.76 (m, 8 H), 8.15−8.37 (m, 6 H), 7.85−8.04 (m, 10 H), 7.40−7.73 (m, 16 H), 7.25−7.36 (m, 8 H), 6.74−7.03 (m, 6 H), 6.44−6.70 (m, 6 H), 6.30 (d, J = 8.15 Hz, 2 H). ^{13}C NMR (75 MHz, d_6-DMSO): δ 178.4, 160.4, 154.5, 150.5, 149.7, 147.3, 144.5, 136.8, 136.4, 135.1, 133.8, 131.7, 130.8, 129.6, 127.3, 126.7, 124.2, 121.3, 121.4, 117.8, 100.9, 99.4. ES-MS *m*/*z*: 1654.2 (M − PF$_6$)$^+$, 1242.9 (M − PF$_6$ − Ru(bpy)$_2$)$^+$, 755.9 (M − 2PF$_6$)$^{2+}$. Anal. Calcd for $C_{92}H_{62}F_{12}N_{10}P_2Ru_2$: C, 61.40; H, 3.45; N, 7.79. Found: C, 61.27; H, 3.51; N, 7.71.

Complex 6. A 25% yield from 1,5-bis(ethynyl)anthracene was achieved. ^{1}H NMR (300 MHz, d_6-DMSO): δ 6.32 (d, J = 8.25

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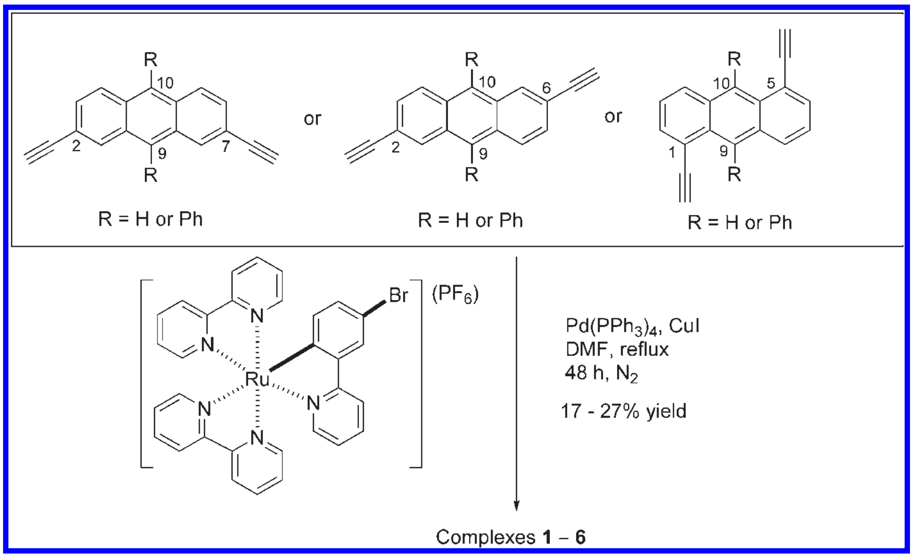
(61) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, 3334.

(62) Constable, E. C.; Holmes, J. M. *J. Organomet. Chem.* **1986**, *301*, 203.

(63) Coudret, C.; Fraysse, S.; Launay, J.-P. *Chem. Commun.* **1998**, 663.

(64) Fraysse, S.; Coudret, C.; Launay, J.-P. *J. Am. Chem. Soc.* **2003**, *125* (19), 5880.

Scheme 1. Synthesis of the Binuclear Ruthenium Complexes through a Sonogashira Cross-Coupling Reaction



Hz, 2 H), 6.65−6.82 (m, 6 H), 7.04−7.15 (m, 6 H), 7.26−7.70 (m, 8 H), 7.84−7.92 (m, 14 H), 7.92−8.15 (m, 10 H), 8.45−8.76 (m, 8 H). ^{13}C NMR (75 MHz, d_6-DMSO): δ 178.0, 155.5, 151.3, 149.4, 148.1, 145.2, 138.8, 137.5, 136.2, 134.8, 133.2, 132.4, 130.9, 129.8, 129.0, 125.2, 122.7, 120.1, 114.1, 101.2, 99.1. ES-MS m/z: 1501.7 [M − (PF$_6$)]$^+$, 1089.5 [M − PF$_6$ − Ru(bpy)$_2$]$^+$, 679.2 [M − 2PF$_6$]$^{2+}$. Anal. Calcd for $C_{80}H_{54}F_{12}N_{10}P_2Ru_2$: C, 58.33; H, 3.28; N, 8.51. Found: C, 58.06; H, 3.54; N, 8.74.

Results and Discussion

As mentioned earlier, we report on the synthesis and electrochemical and spectroscopic characterization of six homobinuclear cyclometalated ruthenium complexes, **1**−**6** (Chart 1). Significant electronic communication between the metallic units, through the different anthracene cores, was evidenced not only by cyclic voltammetry but also by spectroscopic measurements in the NIR region when the mixed-valence species were electrochemically generated.

The ability of anthracene to mediate electronic effects has been previously reported and frequently justified, in a qualitative way, by the possibility of a mesomeric structure.[65,66] However, all previous reports have focused on anthracene derivatives substituted on C9 and C10 since 9,10-diethynylanthracene is readily available, either from the 9,10-bis-TMS-anthracene[67] or the 9,10-bis-dimethylcarbinolanthracene.[68] In this paper, we have systematically studied the influence of the substitution at different positions of the anthracene core, such as C2−C6, C2−C7, and C1−C5, on the electronic communication between the redox units (see Chart 1).

Syntheses and Characterization. As illustrated in Scheme 1, the homobinuclear ruthenium complexes **1**−**6** were synthesized from the appropriate substituted bis(ethynyl)anthracene derivative and the brominated mononuclear ruthenium complex by a palladium-catalyzed cross-coupling reaction.

The preparation of the binuclear ruthenium complexes, **1**−**6**, consisted of the separate synthesis of the anthracene and diphenylanthracene precursors and the mononuclear complex, [Ru(bpy)$_2$(Br-phpy)](PF$_6$), by following synthetic procedures described in the literature for similar compounds.[69,70] The brominated cyclometalated mononuclear ruthenium complex, [Ru(bpy)$_2$(Br-phpy)](PF$_6$), was prepared as previously reported.[63] Substituted diaminoanthraquinones were converted into the dibromo derivatives via Sandmeyer reaction (Scheme 2, step a).[57,58] Diphenylanthracene cores were obtained by reaction of the appropriate dibromoanthraquinones[55,58,59] with phenyl magnesium bromide (Scheme 2, step b) in anhydrous tetrahydrofuran at room temperature and subsequently treated with Zn powder in an aqueous acetic acid solution at 120 °C.[56] Sonogashira coupling between the dibromo-9,10-diphenylanthracene derivatives and (trimethylsilyl)acetylene afforded the corresponding di-(trimethylsily)-9,10-diphenylanthracenes[60,61] (Scheme 2, step c), which were readily deprotected (Scheme 2, step d) by stirring the mixture for 2 h in the presence of 2 equiv of tetrabutylammonium fluoride in tetrahydrofuran to eventually yield the desired bis(ethynyl)-9,10 diphenylanthracene cores.[60,61] Anthracene bridging ligands were prepared by reduction of the anthraquinone cores with sodium borohydride (Scheme 2, step e) as previously reported.[57,58] Preparation of the bis(ethynyl)anthracene derivatives was performed by a synthetic methodology analogous to that employed to afford the bis(ethynyl)-9,10-diphenylanthracene derivatives described above.

Electrochemistry. Electrochemical studies of the homobinuclear compounds, **1**−**6**, were initially performed in methylene chloride solution containing 0.1 M n-Bu$_4$NPF$_6$ as a supporting electrolyte. All of the homobinuclear ruthenium complexes investigated displayed similar electrochemical behavior in this medium. Whereas the mononuclear analog [Ru(bipy)$_2$(phpy)](PF$_6$) displays a single reversible oxidation wave on the anodic scan at E^0 = 0.591 V versus Ag/AgCl (inset Figure 1), two-reversible metal-based one-electron oxidation waves are observed

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(65) Taylor, P. N.; Wylie, A. P.; Huuskonen, J.; Anderson, H. L. *Angew. Chem., Int. Ed.* **1998**, *37*, 986.

(66) Piet, J. J.; Taylor, P. N.; Anderson, H. L.; Osuka, A.; Warman, J. M. *J. Am. Chem. Soc.* **2000**, *122*, 1749.

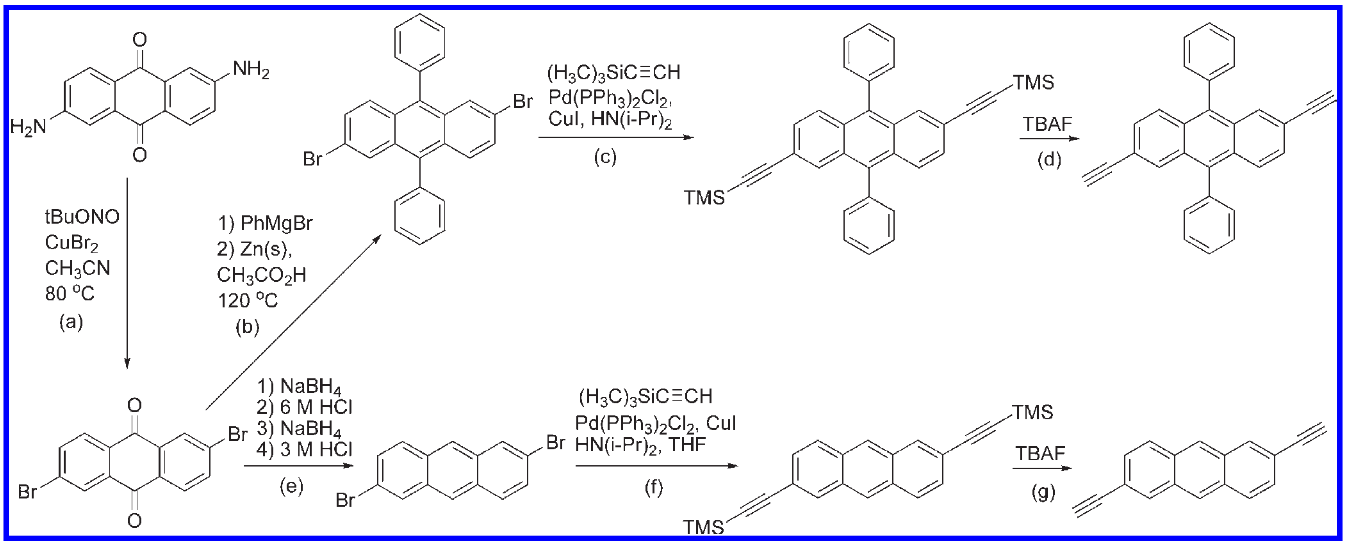
(67) Kobayashi, E.; Jiang, J.; Furukawa, J. *Polym. J.* **1990**, *22*, 266.

(68) Thorand, S.; Krause, N. *J. Org. Chem.* **1998**, *63*, 8551.

(69) Svorstol, I.; Høiland, H.; Songstad, J. *Acta Chem. Scand. B* **1984**, *38*, 885.

(70) Fraysse, S.; Coudret, C.; Launay, J.-P. *J. Am. Chem. Soc.* **2003**, *125* (19), 5880.

Scheme 2. Overall Synthetic Pathway to Obtain Anthracene and Diphenylanthracene Derivatives



for all of the binuclear ruthenium complexes investigated (Figures 1 and 2).

In addition, a quasi-reversible anodic process ascribed to the formation of the diphenylanthracene radical cation, $DPA^{\bullet+}$, occurs at + 1.65 V versus Ag/AgCl (Figure 1). The formal potentials of the metal-based oxidation processes for compounds **1**−**6** are summarized in Table 1. The first oxidation occurs at lower potentials for all of the binuclear complexes, **1**−**6**, compared to the mononuclear complex, $[Ru(bpy)_2(phpy)](PF_6)$. On the other hand, the second anodic process becomes more difficult in all cases.

The splitting displayed in the metal-based anodic oxidations, separated into two one-electron waves, is a clear indication of the stability of the electrochemically generated mixed-valence intermediates.

Particularly for **1**, the second one-electron oxidation occurs at a potential that is 264 mV more positive than the first monoelectronic couple, reflecting a strong degree of electronic communication between the redox units.

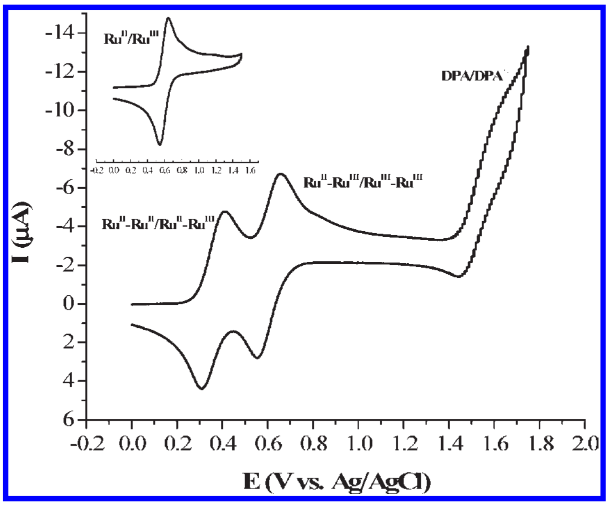


Figure 1. Cyclic voltammetry of the homobinuclear complex **1** in CH_2Cl_2/0.1 M n-Bu_4NPF_6 at a glassy carbon electrode (d = 3 mm). Scan rate: 100 mV s^{-1}. Ref.: Ag/AgCl. Counter electrode: Platinum wire. Inset: Cyclic voltammetry of the mononuclear complex, $[Ru(bipy)_2(phpy)]$-(PF_6) for comparison.

The effectiveness of the ET process is related to the stability of the mixed-valence state and can be discussed on the basis of the comproportionation constant K_c (eq 1), which can be determined from electrochemical measurement of the difference in formal potentials ($\Delta E^{0\prime}$) of the two one-electron oxidation waves and can be expressed as

$$M^n + M^{(n-2)} \rightleftarrows 2M^{(n-1)}$$

$$K_c = 10^{\Delta E/59\mathrm{mV}} = [M^{(n-1)}]^2/[M^n][M^{(n-2)}] \qquad (1)$$

The K_c values determined from electrochemical data evidence the stability of the electrochemically generated mixed-valence species. A shorter metal−metal distance would be anticipated for the dinuclear complexes substituted on C2 and C7 of the anthracene cores with respect to the analogous complexes substituted on C2 and C6. The relatively weaker electronic coupling for the anthracene linkages substituted on C1 and C5 is attributed, at least in part, to steric hindrance, preventing coplanarity of the metallic moieties and the central anthracene core. All of these aspects are borne out by the electrochemical data (Table 1), where it is evident that the 2,7 substitution gives rise to the strongest interaction (largest $\Delta E^{0\prime}$ values), while the 1,5 substitution gives rise to the smallest differences.

Dichloromethane was initially employed as a solvent to perform cyclic voltammetric measurements. Its weakly coordinating properties, particularly its very weak ability to act as a donor, favors its use for studies of inorganic/coordination compounds. However, its low dielectric constant, 8.9 at 25 °C,[68] can cause some restrictions on its general use as a solvent when ionic species are involved. Salts of small cations and anions are generally insoluble in this solvent, whereas salts with cations containing large aliphatic substituents are readily soluble in dichloromethane but are known to be only weakly dissociated.[69] Owing to the low degree of dissociation of salts in this solvent, a considerable fraction of the dissolved salts will exist as various ion-paired species.

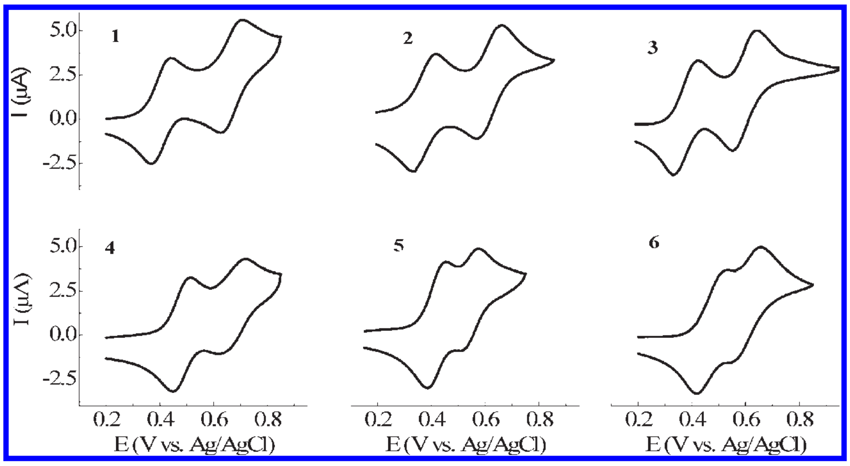


Figure 2. Cyclic voltammetry of the homobinuclear complexes, **1**−**6**, in CH_2Cl_2/0.1 M *n*-Bu_4NPF_6 at a glassy carbon electrode (d = 3 mm). Scan rate: 100 mV s^{-1}. Ref.: Ag/AgCl. Counter electrode: Platinum wire.

Table 1. Electrochemical Data for the Homobinuclear Compounds[a] Including the Mononuclear $[Ru(bpy)_2(phpy)](PF_6)$ Complex for Comparison

compound	$E_1^{0\prime}$ (V)	$E_2^{0\prime}$ (V)	$\Delta E^{0\prime}$ (mV)	K_C
2,7Ru-9,10-DPA, **1**	0.404	0.668	264	2.9×10^4
$2,7Ru_2$-9,10-AN, **2**	0.389	0.647	258	2.3×10^4
$2,6Ru_2$-9,10-DPA, **3**	0.410	0.654	244	1.4×10^4
$2,6Ru_2$-9,10-AN, **4**	0.480	0.670	190	1.7×10^3
$1,5Ru_2$-9,10-DPA, **5**	0.419	0.540	121	1.1×10^2
$1,5Ru_2$-9,10-AN, **6**	0.474	0.602	128	1.5×10^2
$[Ru(bpy)_2(ppy)]$	0.591			

[a] Potential data in volts versus Ag/AgCl are from single scan cyclic voltammograms recorded in CH_2Cl_2/0.1 M *n*-Bu_4NPF_6.

Although $\Delta E^{\circ\prime}$ values of compounds containing equivalent redox sites linked by a bridging ligand have been commonly employed as an indication of the strength of the electronic interaction between electron transfer sites, it is well-known that the effects, not only of the solvent but also of the counterion on $\Delta E^{\circ\prime}$ values (and corresponding comproportionation constants, K_c) may be large, and systematic investigations of the combined medium effects in low-polarity solvents have been reported.[69−77] In order to address several medium effects that could be affecting our measurements, we extended our initial studies in dichloromethane for **2** to other solvent/electrolyte media (Figure 3). Specifically, we also employed acetonitrile and DMF as solvents and chloride, PF_6^-, and $[B(C_6F_5)_4]$ as anions with tetra-*n*-butyl ammonium as the cation in all cases. A set of electrochemical measurements was performed, and the results obtained are summarized in Table 2.

Some previous electrochemical studies with mono- and binuclear ruthenium(II) complexes have reported on the dependence of the redox potentials of the complexes studied on the anion of the supporting electrolyte.[75] Ion pairing between the cationic complex and electrolyte anion would be expected to result in changes in the separation between the formally $Ru^{II}Ru^{II}/Ru^{II}Ru^{III}$ and $Ru^{II}Ru^{III}/Ru^{III}Ru^{III}$ couples and could be correlated with differences in ion-pairing effects.[6,7,12,19,50,67,75−77] In this sense, it should be pointed out that the largest $\Delta E^{0\prime}$ values have been found when low donor solvents have been employed in the presence of weakly coordinating anions used as supporting electrolytes, such as *n*-Bu_4N-$[B(C_6F_5)_4]$. In contrast, the use of small anions such as chloride led to a significant decrease in the $\Delta E^{0\prime}$. On the other hand, changing from a low polarity solvent to a higher polarity solvent, such as acetonitrile, shows the effects of solvation over ion pairing and leads to smaller $\Delta E^{0\prime}$ values. Furthermore, the overall change in $\Delta E^{0\prime}$ is mostly due to the shift of the second oxidation processes.

This could be rationalized by taking into account the existence of electrostatic interactions in which the greater positive charge density of the dicationic species would result in higher ion-pairing effects.[53,55]

UV/Vis/NIR Spectroelectrochemistry

The UV−vis−NIR spectra of the binuclear compounds were recorded. The absorption spectra of the binuclear ruthenium complexes exhibited very intense bands near 300 nm (black line, Figure 4) assigned to ligand-centered (LC) π−π^* transitions, and moderately intense bands located in the visible region from 350 to 600 nm ascribed to metal-to-ligand charge-transfer (MLCT) transitions. The mixed-valence species, derived from all of the compounds, were electrochemically generated and their formation followed by absorption spectroscopy. Thus, a stepwise coulommetric titration was performed on a 1 mM solution of compounds **1**−**6** in $CDCl_3$/0.1 M *n*-Bu_4NPF_6, and absorption spectra were regularly recorded during the oxidation process. Figures 4 and 5 show the evolution of the spectra of compounds **3** and **5**, respectively, during the electrochemical oxidation process. The characteristic MLCT broad bands progressively decreased in amplitude, and a new band, centered at around 750 nm, emerged. This band was ascribed to ligand-to-metal charge-transfer transitions (LMCT). This band reached its maximum intensity when complete oxidation to the $Ru^{III}Ru^{III}$ form was achieved. In addition, and particularly important in the present context, broad IVCT transitions were found in the NIR region for all of the

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(71) Algra, G. P.; Balt, S. *Inorg. Chem.* **1981**, *20*, 1102.

(72) Ito, K.; Iwamoto, E.; Yamamoto, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2143.

(73) Abbott, A. *Chem. Soc. Rev.* **1993**, 435.

(74) Pospíšil, L.; King, B. T.; Michl, J. *Electrochim. Acta* **1998**, *44*, 103.

(75) Yeomans, B. D.; Kelso, L. S.; Tregloan, P. A.; Keene, F. R. *Eur. J. Inorg. Chem.* **2001**, 239.

(76) Hupp, J. T. *Inorg. Chem.* **1990**, *29*, 5010.

(77) Ruiz, J.; Astruc, D. *C. R. Acad. Sci. Paris* **1998**, *2*, 21.

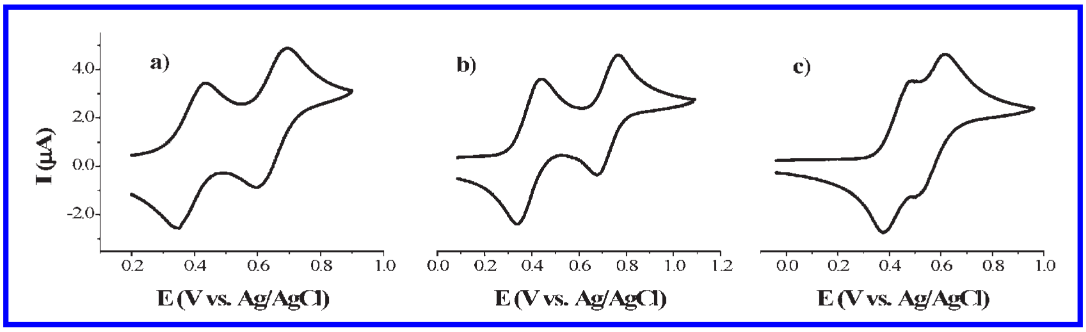

Figure 3. Cyclic voltammetry of the homobinuclear complex, **2**, in CH_2Cl_2 (a) 0.1 M *n*-Bu_4NPF_6, (b) 0.1 M *n*-$Bu_4N[B(C_6F_5)_4]$, and (c) 0.1 M *n*-Bu_4NCl at a glassy carbon electrode (d = 3 mm). Scan rate: 100 mV s^{-1}. Ref: Ag/AgCl. Counter electrode: platinum wire.

Table 2. Electrochemical Data for the Homobinuclear Compound, **2**[a] in Three Different Solvents

2,7Ru$_2$-9,10-AN, **2**	$E_1^{0\prime}$ (V)	$E_2^{0\prime}$ (V)	$\Delta E^{0\prime}$ (mV)	K_C
CH_2Cl_2/*n*-Bu_4NPF_6	0.389	0.647	258	2.3×10^4
CH_2Cl_2/*n*-Bu_4NCl	0.414	0.530	116	9.2×10^1
CH_2Cl_2/*n*-$Bu_4N[B(C_6F_5)_4]$	0.400	0.752	352	2.0×10^6
CH_3CN/*n*-Bu_4NPF_6	0.419	0.575	166	4.4×10^2
CH_3CN/*n*-Bu_4NCl	0.405	0.497	92	3.6×10^1
CH_3CN/*n*-$Bu_4N[B(C_6F_5)_4]$	0.402	0.640	238	1.1×10^4
DMF/*n*-Bu_4NPF_6	0.415	0.563	148	3.2×10^2
DMF/*n*-Bu_4NCl	0.418	0.520	102	5.3×10^1
DMF/*n*-$Bu_4N[B(C_6F_5)_4]$	0.396	0.658	262	2.8×10^4

[a] Potential data in volts versus Ag/AgCl are from single scan cyclic voltammograms.

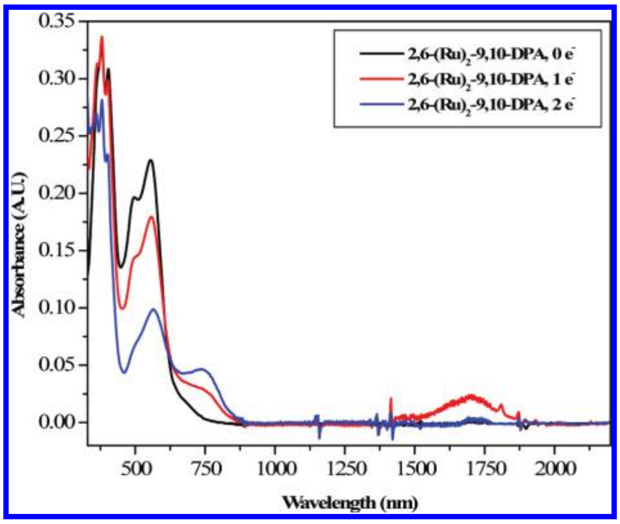

Figure 4. UV−vis−NIR spectra in $CDCl_3$ of 2,6(Ru)$_2$-9,10-DPA before oxidation (black line), after half-oxidation (1 electron, red line), and after full oxidation (2 electrons, blue line).

bimetallic compounds investigated. The IVCT bands were centered at 1580 (compound **1**), 1520 (compound **2**), 1725 (compound **3**), 1638 (compound **4**), 1322 (compound **5**), and 1310 (compound **6**), as summarized in Table 3. The intensity of these bands increased continuously during the oxidation process until complete formation of the mixed valence compounds was achieved upon consumption of one electron. These transitions are assigned to bridge-mediated intramolecular electron transfer when the mixed-valence species were formed. These IVCT transitions are absent in the $Ru^{II}Ru^{II}$ complexes and entirely disappear in the $Ru^{III}Ru^{III}$ species (i.e., the fully oxidized forms), as shown in Figures 4 and 5. Analyses of the IVCT bands are presented in Table 3, in which bandwidths are compared with the theoretical values expected from Hush's expression[79] $\Delta\nu_{1/2} = (2310\nu_{max})^{1/2}$. Experimental values were of the same order of magnitude for all of the complexes studied, **1**−**6**, and slightly narrower than predicted by Hush's theory, suggesting the categorization of these complexes as class II mixed-valence species according to the Robin and Day classification.

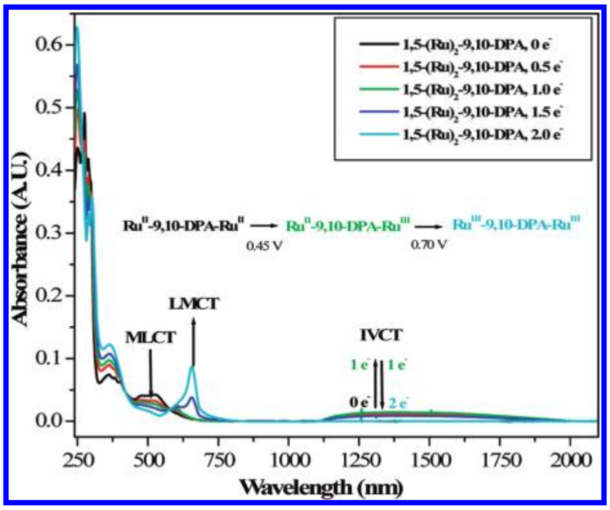

Figure 5. UV−vis−NIR spectra in $CDCl_3$ of 1,5(Ru)$_2$-9,10-DPA before oxidation (black line), after half-oxidation (1 electron, green line), and after full oxidation (2 electrons, bright blue line).

Table 3. Intervalence Charge Transfer (IVCT) Transitions and Experimental and Theoretical Bandwidth Values for the Homobinuclear Ruthenium Compexes, **1**−**6**

compd	λ (nm)	$\Delta\nu_{1/2(exp)}$[a]	$\Delta\nu_{1/2(theo)}$[b]	Γ[c]
2,7Ru$_2$-9,10-DPA, **1**	1580	2740	3825	0.28
2,7Ru$_2$-9,10-AN, **2**	1520	3330	3900	0.15
2,6Ru$_2$-9,10-DPA, **3**	1725	2520	3660	0.31
2,6Ru$_2$-9,10-AN, **4**	1638	2615	3755	0.30
1,5Ru$_2$-9,10-DPA, **5**	1322	3900	4180	0.07
1,5Ru$_2$-9,10-AN, **6**	1310	4050	4200	0.04

[a] Full width at half-height in cm^{-1} (experimental). [b] Full width at half-height in cm^{-1} computed from Hush's equation. [c] Γ is estimated from eq 2.

The Γ values, a parameter introduced by Sutin[40,78] and co-workers to provide an estimation of the electron coupling in mixed-valence species, are also included in Table 3. Such a parameter has been calculated from eq 2 and is commonly used as a measure of the delocalization degree

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(78) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.

in mixed-valence complexes. Its value is readily calculated from the deviation of the bandwidth from its theoretical value as specified in eq 2. Values within the range $0 < \Gamma < 0.5$ are expected for class II mixed-valence species, whereas larger Γ values are expected for the most delocalized systems.

$$\Gamma = 1 - \Delta\nu_{1/2\mathrm{exp}}/\Delta\nu_{1/2\mathrm{theo}} \qquad (2)$$

Thus, for weakly coupled (localized) class II systems, Γ varies from 0 to 1.0. Its value progressively increases, in the same direction as the electronic coupling, exhibiting values in the range $0.1 < \Gamma < 0.5$ for moderately coupled class II systems.

Conclusions

We have synthesized and characterized, via electrochemical and spectroscopic techniques, a family of anthracene-bridged binuclear ruthenium complexes whose degree of metal−metal interactions could be modulated by changes in the nature of the bridge and substitution pattern. We have also studied the dependence of the $\Delta E^{0\prime}$ values for the oxidation processes of homobinuclear mixed-valence complexes on the medium. As has been previously pointed out, the comproportionation constants estimated from electrochemical data can be used as an indication of the thermodynamic stability of the mixed-valence species. However, as previously reported by Keene and co-workers, particular caution should be taken when trying to establish relationships between the K_c values and the strength of the metal−metal electronic communication mediated by a bridging ligand since a number of experimental factors (such as the solvent and supporting electrolyte) can affect, as we have shown, the measured redox potentials for these oxidation processes.[4,11] As a result, several discrepancies have been encountered when comparing electrochemical and spectroscopic data in order to establish the extent of localization/delocalization through the anthracene-bridged π-conjugated systems employed in the binuclear ruthenium complexes (**1**−**6**) described herein. In this sense, the analysis of IVCT bands provides a more reliable estimate of the extent of interaction through the Γ parameter (within the range $0 < \Gamma < 0.5$ in all the cases), which leads us to conclude that the bimetallic complexes investigated belong to class II in the Robin and Day classification.

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Supporting Information Available: Synthetic procedure and characterization of compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(79) (a) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391. (b) Hush, N. S. *Electrochim. Acta* **1968**, 1005.