

and an ortho-metalated dppe. A second chelated dppe completes the coordination sphere around Rh(1), which adopts a pseudooctahedral geometry, while the Rh(2) atom is in a distorted trigonal-bipyramidal geometry. The Rh-Rh bond distance [2.7331 (8) Å], which in dirhodium(II,II) complexes is the most salient feature, lies at the top range of distances observed in this class of compounds.¹ The reduced number of bridging ligands and the constraining effect of the bridging ortho-metalated dppe can explain the significant lengthening of the Rh-Rh bond distance in the title complex. A similar elongation of the metal-metal separation [2.770 (3) Å] has been recently found in the complex $[\text{Rh}_2(\text{dppm})_2(\text{C}_6\text{H}_5)_2(\text{C}_6\text{H}_4)\text{P}]_2\text{Cl}_2$,¹⁶ where two ortho-metalated triphenylphosphines are present. Each diphosphine occupies an equatorial and an axial site. The Rh-P distances range from 2.195 (2) to 2.367 (2) Å, with the longest Rh-P trans to the Rh-Rh bond, and are comparable with the values found in other dirhodium(II,II) derivatives.¹

The values of 163.06 (6) and 157.2 (2)° for the Rh(2)-Rh(1)-P(4) and N(1)-Rh(2)-P(1) bond angles are clearly imposed by the bidentate coordination of the dppe groups, which are then responsible for the distortion from the normal octahedral and square-pyramidal geometry around Rh(1) and Rh(2), respectively. All the bridging ligands are not planar with values of 10.0 (2), 10.2 (3), and 21.4 (3)° for the P(2)-Rh-Rh-C, O-Rh-Rh-O, and N-Rh-Rh-N torsion angles, respectively. The trifluoroacetate group is bonded to the dimetal unit by different Rh-O distances [Rh(1)-O(1) = 2.235 (5) Å; Rh(2)-O(2) = 2.147 (5) Å] with the longest value reflecting the trans influence of the C(26) ortho-metalated carbon atom. The formamidinate fragment is bonded to the dirhodium unit in the usual way, namely $\sigma, \sigma\text{-N, N}'$ with delocalized double bonds and by different Rh-N distances, the shortest being associated with the greatest deviation of the N(1)-Rh(2)-P(1) angle from linearity.

Although the mechanism of the reaction remains obscure, steric and electronic reasons might account for the ortho-metalation of one dppe. The formation of the title complex can be rationalized on the basis of initial bis-chelate dppe derivative generation. Given the steric demand of the phenyl and *p*-tolyl groups, one of the phenyl groups closely approaches the adjacent rhodium atom leading to formal transfer of an ortho proton to a formamidinate group followed by ortho-metalation and elimination of formamide from the lantern structure.

It is worthwhile to mention that the analogous reaction of $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4$ with dppe gives an insoluble material,¹⁷ which, on the basis of analytical and IR data, was suggested to be a simple bis-axial adduct, while the complex $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ gives with the diphosphine dmpe (dmpe = 1,1-bis(dimethylphosphino)ethane) infinite zigzag chains of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ units linked by the bidentate ligands.¹⁸ The great tendency of dppe to form chelated complexes associated with the facile displacement of the trifluoroacetate groups from the lantern structure disfavor in the reaction reported here the formation of polymeric materials or simple axial adducts.

In conclusion the complex reported here shows some peculiar features. In fact, it represents the first example of ortho-metalation of a diphosphine across a metal-metal bond as well as the first report of a dirhodium(II,II) complex in which the Rh_2^{4+} core is supported by three different bridging ligands. A final comment concerns the formal oxidation state of the two rhodium atoms. The bridging trifluoroacetate and formamidinate as well as the ionic trifluoroacetate groups contribute three negative charges to the rhodium system, which charges are equally shared between the two rhodium atoms. Furthermore the ortho-metalated phenyl ring contributes one negative charge to Rh(2) so that the total charge on the two metal centers became unequally shared. On these bases, the title complex, owing to the asymmetric ar-

angement of the ligands around the two rhodium atoms, may be best described as a formally mixed-valent complex with non-integral oxidation states.

Acknowledgment. Financial support from the Ministero dell'Università e della Ricerca Scientifica is gratefully acknowledged.

Supplementary Material Available: A fully numbered ORTEP diagram and Tables SI-SV, listing full crystal data, nonessential atomic distances and angles, hydrogen atom parameters, temperature factors, and complete positional parameters (10 pages); a table of calculated and observed structure factors (33 pages). Ordering information is given on any current masthead page.

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Photoredox Pathways to Spatially Restricted Metallopolymeric Films

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Received August 9, 1991

Introduction

There now exists an extensive body of synthesis¹⁻³ and applications-based²⁻⁴ chemistry for redox-active metallopolymeric films. The applications include electrochemical catalysis, energy conversion, electrochromic displays, analysis, and molecular and ionic sensing.²⁻⁴ Films for these purposes are most commonly assembled via electrochemically initiated radical polymerization pathways or, less often, by simple spin casting of preformed metallopolymers (or metal-free polymer backbones). Both approaches lead to films of more or less uniform composition, which effectively cover the entire available exposed surface support area.

In pursuit of additional applications (remote optical sensing and advanced electrochromics), we have devised an additional method for assembling films. The new approach, which is based on simple redox quenching processes following photochemical excitation, was designed to meet three specific requirements: (1) film assembly on transparent surfaces, (2) spatially selective assembly, and (3) assembly, if necessary, on insulating surfaces. Elements 1 and 2 were deemed desirable for electrochromic applications in which small multicomponent (multicolor) electrochromic images (alphanumerics, etc.) might be expanded and displayed via simple light projection through a transparent electrode surface. Element 3 (together with one or both of the others) could prove exceptionally important in analytical applications (for example, liquid chromatography detection) in which metallopolymer luminescence would be employed as a reporter for specific film-bound analytes. (Note that metallopolymer luminescence is often extensively or completely quenched (by energy transfer) when metallic or semiconducting support surfaces are used.) While some of these objectives can be achieved with existing synthetic or assembly methods, for any given system it is difficult to achieve all three simultaneously. As indicated below, however, we have been reasonably successful in reaching these goals by employing a straightforward photoredox approach.

Experimental Section

Materials. Reagent grade acetonitrile was used as received. Tetrabutylammonium perchlorate (TBAP) was purchased from GFS Chem-

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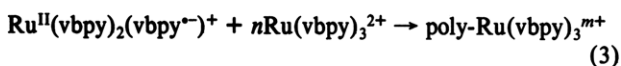
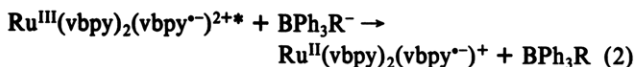
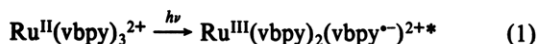
icals. [Ru(vbpy)₃](PF₆)₂ (vbpy is 4-methyl-4'-vinylbipyridine) and [Ru(bpy-pyr)₃](PF₆)₂ (bpy-pyr is 4-(2-pyrrol-1-ylethyl)-4'-methyl-2,2'-bipyridine) were prepared by literature methods.^{5,6} Tetramethylammonium salts of several triphenylalkylborates⁷ (alkyl = *n*-butyl, *sec*-butyl, *n*-hexyl, and benzyl) were generously provided by Dr. Peter Gottschalk of Mead Imaging. Methylviologen dichloride was purchased from Aldrich and metathasized to the hexafluorophosphate form by addition of excess NH₄PF₆ to the chloride salt in water.

Measurements. Cyclic voltammetry experiments were generally carried out in a one compartment cell containing a conductive glass (antimony-tin oxide coated) working electrode, a platinum-wire counter electrode, a saturated calomel reference, and 0.1 M TBAP as supporting electrolyte. Measurements were made with a PAR 174A potentiostat and a Houston Omnigraphics X-Y recorder. Photolysis experiments utilized a 450-W Hg-Xe lamp with UV cutoff filter or, in a few instances, a 500-mW (all lines) argon ion laser. Photolysis solutions typically contained from 1 to 5 mM of metal complex and from 100 to 200 mM of quencher in acetonitrile as solvent.

Results and Discussion

In devising an alternative method of film assembly, we sought to exploit two features often associated with monomeric transition-metal complexes—namely, their intense chromophoric and long-lived excited-state characteristics and their propensity to undergo reversible ligand- and metal-based electron transfer. In electropolymerization reactions, the necessary radical initiator species are generated by ligand-localized oxidation or reduction at an electrode/solution interface; films are obtained when the resulting oligomers reach sufficient size to become insoluble and deposit onto the electrode surface.¹⁻⁶ We reasoned that radicals could also be generated photochemically by irreversible electron transfer quenching of monomer excited states. As an example, a coordinated vbpy radical anion might be obtained by reductive quenching of Ru(vbpy)₃²⁺ by any of several triphenylalkylborate species^{5c} (Scheme I). As suggested by Scheme I, quenching is irreversible because of rapid decomposition of BPh₃R.^{7,9} The remaining Ru^{II}(vbpy)₂(vbpy⁻)⁺ complex should then be capable of initiating polymerization.

Scheme I



We find experimentally that visible-region photolysis of an acetonitrile solution of Ru(vbpy)₃²⁺ and BPh₃R⁻, sandwiched between conductive glass and ordinary glass plates (ca. 1-mm spacing), leads within several minutes (Ar⁺ laser source) or a few hours (Hg-Xe source) to a readily visible polymeric coating on the plate closest to the light source.⁸ The film color (orange) and absorption spectrum (λ_{max} ≈ 470 nm) match those found for electrochemically grown poly-Ru(vbpy)₃²⁺. Consistent with the proposed redox quenching mechanism, films are obtained most

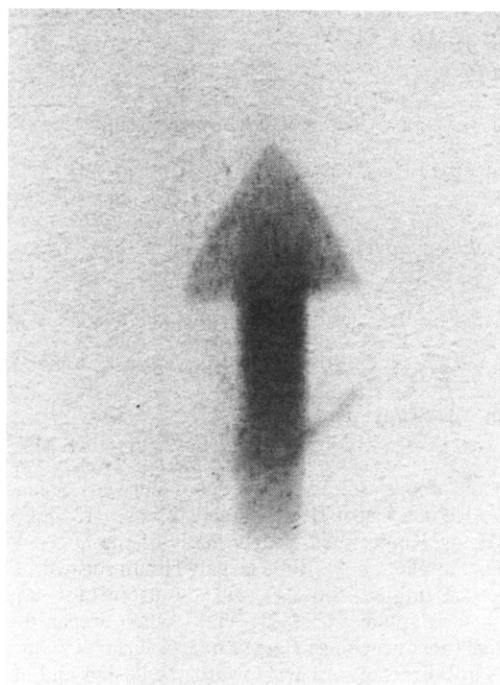


Figure 1. Spatially structured film of poly-Ru(vbpy)₃^{m+} grown on antimony-tin oxide coated glass via Scheme I. (Structure dimensions are 12 mm by 5 mm.)

readily from solutions containing triphenyl-*n*-hexylborate (most easily oxidized quencher), but not at all from solutions containing tetraphenylborate (most difficult quencher to oxidize⁷). As shown by Figure 1, spatially restricted photolysis leads to a fairly well-defined polymeric image on the transparent surface. Control experiments in the absence of quencher or in the absence of vinyl substituents on the metal complex do not yield films.

Subsequent electrochemical studies (conductive glass surfaces) have shown the films to be electroactive, with a reversible peak near +1.35 V vs the SCE. From previous work,⁵ the peak can be unambiguously assigned as the polymer-based Ru(II/III) couple. Consistent with that assignment, spectral studies with thin films (ca. 10 molecular monolayer equiv, based on ε(470) = 14 000 M⁻¹ cm⁻¹) show that the polymer can be completely and reversibly bleached (metal-to-ligand charge-transfer region) by holding the electrode potential at +1.6 V. Unfortunately, thicker films (ca. 200 monolayer equiv), which display more intense coloration, are only partially bleached (ca. 20%) by electrochemical polarization.¹⁰ Evidently for these thicker films only a small fraction of the polymer can be addressed electrochemically. It is interesting to note, however, that thick films can be bleached completely by using a solution-phase oxidant (aqueous Ce⁴⁺).

Electroactive film formation also proved possible with a pyrrole-functionalized chromophore, Ru(bpy-pyr)₃²⁺, together with a known reversible oxidative quencher, MV²⁺.^{10,11} Although we have not explored the question of mechanism in any detail,¹² Scheme II is fully consistent with proven photochemical¹⁰ and electrochemical^{2,6} reaction pathways. It is interesting to note that the apparent availability of one or more photon-wasting back-reactions (eq 9a and/or eq 9b) does not preclude film formation.¹¹ Like poly-Ru(vbpy)₃ⁿ⁺, the photochemically assembled poly-

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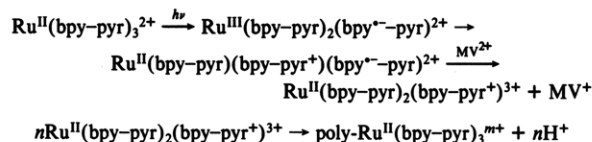
(8) With the argon ion laser source, film formation was sometimes also observed on the plate furthest from the source.

(9) A few experiments were also done with tetramethylphenylenediamine, a reversible quencher. Somewhat surprisingly (in view of the ample opportunity for short-circuiting back-electron-transfer), reasonable metallopolymeric films were still obtained.

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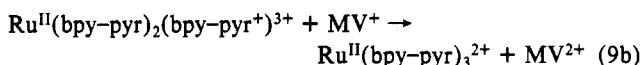
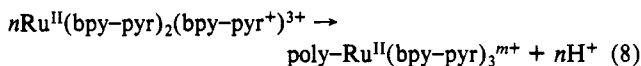
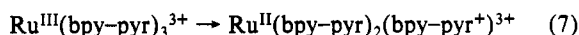
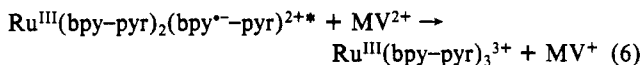
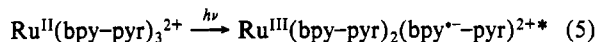
(11) Note also ref 9.

(12) We have not necessarily ruled out, for example, an alternative reaction sequence whereby the methylviologen captures a secondary charge-transfer state:



Ru(bpy-pyr)₃²⁺ films exhibit reversible metal-centered redox behavior at about +1.4V.

Scheme II



As noted above, thicker films (vbpy-derived) are not fully electroactive in a direct electrochemical sense. If that problem cannot be overcome, then clearly many of the hoped for electrochromic applications will be largely circumscribed. Even so, the photoassembled films should be useful for analytical (fluorescence) applications—especially when prepared on nonconductive (nonquenching) glass or quartz surfaces. Our current interests are directed, in part, toward the design and assembly of chemically functionalized films and film-precursor complexes suitable for binding and detection of specific ions and molecules. With appropriate modifications, the photoredox approach might also provide an interesting entry into *soluble* metallopolymers and copolymers.

Acknowledgment. We thank Mead Imaging and the NSF Materials and Research Center at Northwestern (DMR-8821571) for support of this work. Funds for purchase of the OLIS-modified spectrophotometer were provided by the National Science Foundation through an equipment grant (CHE-8722985) and a Presidential Young Investigator Award (CHE-8552627). J.T.H. acknowledges additional financial support in the form of a Dreyfus Teacher-Scholar Award and a fellowship from the Alfred P. Sloan Foundation.

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Synthesis and Semiconducting Properties of Bridged (Phthalocyaninato)osmium Compounds with Bidentate N-Donor Ligands

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Received September 19, 1991

Monomeric and bridged bisaxially coordinated transition-metal complexes MacML₂ and [MacML]_n with phthalocyanine (Pc), tetrabenzoporphyrine (TBP), 1,2- or 2,3-naphthalocyanine (1,2- or 2,3-Nc), and phenanthrocyanine (Phc) as the macrocycles (Mac), transition metals, e.g. iron or ruthenium, as the central metal atom (M), and bidentate ligands (L), e.g. pyrazine (pyz), tetrazine (tz), and 1,4-diisocyanobenzene (dib), have been systematically investigated by us regarding their semiconducting properties.¹ Doping of the bridged systems [MacML]_n e.g. with

iodine leads to comparatively thermally stable compounds [MacMLI_y]_n with good semiconducting properties ($\sigma_{RT} = \sim 0.1$ S/cm).²

We have shown that PcFe, PcRu, and some of their peripherally substituted derivatives and 2,3-NcFe, depending upon the conditions, react with tetrazine and 3,6-dimethyl-*s*-tetrazine (Me₂tz) to form the corresponding monomers MacM(tz)₂ and bridged compounds [MacM(tz)]_n, respectively.³ In contrast to other bridged systems [PcML]_n (M = e.g. Fe, Ru; L = e.g. pyz, dib) the tetrazine-bridged systems [MacML]_n (L = tz, Me₂tz) already exhibit conductivities $\sigma_{RT} = 0.01$ – 0.1 S/cm without additional external oxidative doping.³

One of the factors responsible for the electrical conductivity in bridged macrocyclic transition-metal complexes is the band gap, which is determined by the energy difference between the LUMO of the bridging ligand and the HOMO of the transition metal-macrocycle.⁴ Therefore, to achieve semiconducting properties in such systems, the metallomacrocycle should contain a high-lying HOMO; in addition, a bridging ligand which has a low-lying LUMO such as tz or Me₂tz should be used.⁵ More detailed investigations about this intrinsic effect^{5,6} have shown that these special semiconducting properties without doping were only observed with tetrazine-bridged systems [MacM(tz)]_n in which the group VIII elements Fe and Ru were used as the central metal atom of the macrocycle. Therefore it is of interest to investigate whether or not the corresponding osmium compound [PcOs(tz)]_n would also exhibit comparable intrinsic semiconducting properties like the corresponding iron and ruthenium systems [PcM(tz)]_n (M = Fe, Ru).

Only recently have we been able to prepare pure osmium phthalocyanine, PcOs, and some of its monomeric bisaxially substituted complexes, e.g. PcOs(py)₂ and PcOs(pyz)₂.⁷ We now report here on the first examples of the bridged oligomeric systems [PcOsL]_n with the bidentate N-donor ligands pyz and tz.

Results and Discussion

PcOs was prepared essentially following our earlier method;⁷ however, the yield could be improved by a slight change in the experimental procedure: *o*-cyanobenzamide is reacted with OsCl₃·H₂O in molten naphthalene, and the crude reaction product is directly extracted with pyridine. As a result, all the PcOsL_x derivatives described before⁷ are converted into soluble PcOs(py)₂ which is isolated by chromatography. From the pure PcOs(py)₂ two pyridine molecules are split off at 400 °C, as indicated by an endothermic differential thermal analysis (DTA) maximum at 360 °C (mass loss 17.5%, calc 18.5%).⁷ The remaining blue-black residue is pure PcOs(II) with an overall yield of 38%.

In order to obtain PcOs(pyz)₂, PcOs is reacted with an excess of pyrazine (1:10) at 80 °C. Extraction of the crude reaction product with chloroform yields PcOs(pyz)₂ in about 60% yield.

Among the routes developed by us for the preparation of [PcFe(pyz)]_n⁸ and [PcRu(pyz)]_n,⁹ respectively, only the method in which one pyrazine molecule is split off thermally from the monomer PcRu(pyz)₂ appeared to be promising for obtaining a homogeneous bridged [PcOs(pyz)]_n. The thermogravimetry (TG)/DTA analyses show that the splitting off of the pyrazine molecules from PcOs(pyz)₂ does not take place in two distinct steps as found in the case of PcRu(pyz)₂.⁹ The first pyrazine

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