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. 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 [Rh2(dpdmmp)2(C6H4)2(C6H4)P]2Cl4,16 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.17

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 phenyl atom. The formamidinate fragment is bonded to the dirhodium unit in the usual way, namely e,e,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 formamidine from the lantern structure.

It is worthwhile to mention that the analogous reaction of Rh2(O2CCH3)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 M02(O2CCH3)4 gives with the diphosphine dppe (dpme = 1,1-bis(dimethylphosphino)ethane) infinite zigzag chains of M02(O2CCH3)4 units linked by the bidentate ligands.18 The general 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 Rh1+ 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 arangement of the ligands around the two rhodium atoms, may be best described as a formally mixed-valent complex with non-integral oxidation states.

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Supplementary Material Available: A fully numbered ORTEP diagram and Tables S1–S7, 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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Introduction

There now exists an extensive body of synthetic1–3 and applications-based4–6 chemistry for redox-active metallopolymers. 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 (alphanumeric, 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. Tetra-butylammonium perchlorate (TBAP) was purchased from GFS Chem-

The proposed redox quenching mechanism, films are obtained most electrochemically grown poly-Ru(vbpy)\(_{12}^+\). Consistent with the plate close to the light spacing, leads within acetonitrile solution of Ru(vbpy), and BPh,R-, sandwiched Rulu''(vbpy)z(vbp~)z+*

Notes

1. We find experimentally that visible-region photolysis of an acetonitrile solution of Ru(vbpy), and BPh,R-, 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. The film color (orange) and absorption spectrum (\(\lambda_{\text{max}} = 470\) nm) match those found for electrochemically grown poly-Ru(vbpy)\(_{20}^+\). Consistent with the proposed redox quenching mechanism, films are obtained most readily from solutions containing triphenyl-n-hexylborate (most easily oxidized quencher), but not at all from solutions containing tetraphenylborate (most difficult quencher to oxidize). 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.

2. 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, 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 \(\epsilon(470) = 14000\) 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. 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 Ce\(^{4+}\)).

Electroactive film formation also proved possible with a pyrrole-functionalized chromophore, Ru(bpy-pyr)\(_2^+\), together with a known reversible oxidative quencher, MV\(^{2+}\). Although we have not explored the question of mechanism in any detail, Scheme II is fully consistent with proven photochemical and electrochemical 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. Like poly-Ru(vbpy)\(_{20}^+\), the photochemically assembled poly-

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

(8) Note also ref 9.
Ru(bpy-pyr)$_2^{2+}$ films exhibit reversible metal-centered redox behavior at about $+1.4$ V.

Scheme II

$$\text{Ru}^2(bpy-pyr)_{2}^{2+} \xrightarrow{\text{h+}} \text{Ru}^3(bpy-pyr)_{2}(bpy-pyr)^{2+} \quad (5)$$

$$\text{Ru}^3(bpy-pyr)_{2}(bpy-pyr)^{2+} + MV^{2-} \rightarrow \text{Ru}^4(bpy-pyr)_{2}^{3+} + MV^{+} \quad (6)$$

$$\text{Ru}^3(bpy-pyr)_{2}^{3+} \rightarrow \text{Ru}^4(bpy-pyr)_{2}(bpy-pyr)^{3+} \quad (7)$$

$$n\text{Ru}^{2+}(bpy-pyr)_{2}(bpy-pyr)^{2+} \rightarrow \text{poly}-\text{Ru}^{2+}(bpy-pyr)_{n}^{2n+} + n\text{H}^{+} \quad (8)$$

$$\text{Ru}^4(bpy-pyr)_{2}^{3+} + MV^{2-} \rightarrow \text{Ru}^4(bpy-pyr)_{2}^{2+} + MV^{+} \quad (9a)$$

$$\text{Ru}^4(bpy-pyr)_{2}^{2+} + MV^{2-} \rightarrow \text{Ru}^4(bpy-pyr)_{2}^{+} + MV^{+} \quad (9b)$$

As noted above, thicker films (bpy-derived) are not fully electroactive in a direct electrochemical sense. If that problem cannot be overcome, then clearly many of the hopes for electrochemical applications will be largely circumscribed. Even so, the photoassembled films should be useful for analytical (fluorescence) applications—especially when prepared on non-conductive (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 metalpolymers and copolymers.

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

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Monomeric and bridged bisaxially coordinated transition-metal complexes [MacML]$_n$ and [MacML$_2$] with phthalocyanine (Pc), tetrabenzoporphyrine (TBP), 1,2- or 2,3-naphthalocyanine (Phe) 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. Doping of the bridged systems [MacML]$_n$ e.g. with iodine leads to comparatively thermally stable compounds [MacML]$_n$, with good semiconducting properties ($\sigma_{RT} = 0.1$ S/cm).

We have shown that PCFe, PdRu, and some of their peripherally substituted derivatives and 2,3-NCFe, depending upon the conditions, react with tetrzine and 3,6-dimethyl-s-tetrazine (Me$_2$tz) to form the corresponding monomers MacM(tz)$_n$, and bridged compounds [MacM(tz)$_n$], respectively. In contrast to other bridged systems [PcML], (M = e.g. Fe, Ru; L = e.g. pyz, dib) the tetrzine-bridged systems [MacML], (L = tz, Me$_2$tz) already exhibit conductivities $\sigma_{RT} = 0.01–0.1$ S/cm without additional external oxidative doping.

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 macrocyclic. Therefore, to achieve semiconducting properties in such systems, the metallopolymers should contain a high-lying HOMO; in addition, a bridging ligand which has a low-lying LUMO such as tz or Me$_2$tz should be used. More detailed investigations about this intrinsic effect have shown that these special semiconducting properties without doping were only observed with tetrzine-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, PoCs, and some of its monomeric bisaxially substituted complexes, e.g. Pcs(py)$_2$ and Pcs(py)$_3$. We now report here on the first examples of the bridged oligomeric systems [PcOsL], with the bidentate N-donor ligands pyz and tz.

Results and Discussion

PoCs was prepared essentially following our earlier method, however, the yield could be improved by a slight change in the experimental procedure: o-cyanobenzamide is reacted with OsCl$_3$H$_2$O in molten naphthalene, and the crude reaction product is directly extracted with pyridine. As a result, all the PoCs$_{L_x}$ derivatives described before are converted into soluble PoCs$_{L_y}$, which is isolated by chromatography. From the pure PoCs$_{L_y}$ 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%). The remaining blue-black residue is pure PoC$_{(II)}$ with an overall yield of 38%.

In order to obtain PoCs$_{L_y}$(pyz)$_2$, PoCs is reacted with an excess of pyrazine (1:10) at 80 °C. Extraction of the crude reaction product with chloroform yields PoCs$_{L_y}$(pyz)$_2$, in about 60% yield. Among the routes developed by us for the preparation of [PcOs(pyz)$_2$], and [PcRu(pyz)$_2$], 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)$_2$]$_n$. The thermogravimetry (TG)/DTA analyses show that the splitting off of the pyrazine molecules from PoCs$_{L_y}$(pyz)$_2$ does not take place in two distinct steps as found in the case of PcRu$(pyz)_2$. The first pyrazine


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