

Multicomponent Supramolecular Devices: Synthesis, Optical, and Electronic Properties of Bridged Bis-dirhodium and -diruthenium Complexes

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Dedicated to Professor Vincenzo Balzani

Keywords: N ligands / Electronic coupling / Electrochemistry / Metal–metal interactions / Optical properties

Four ruthenium- and rhodium-based metal–metal-bonded multicomponent systems have been synthesized, and their absorption, redox, spectroelectrochemical and structural properties have been studied. The absorption spectra of the four bis-dimetallic compounds M_2LM_2 , where L is a bridging ligand and M is rhodium or ruthenium, exhibit very strong bands in the UV, visible and, for the diruthenium species, near-IR region. The low-energy absorption bands are assigned to charge-transfer transitions involving a metal–metal bonding orbital as the donor and an orbital centered on the bis-tetradentate aromatic ligands as the acceptor (metal–metal to ligand charge transfer, M_2LCT). Each compound exhibits reversible bridging-ligand-centered reductions at mild potentials and several reversible oxidation processes. The oxidation signals of the two equivalent dimetallic centers of each bis-dimetallic compound are split, with the splitting – a measure of the electronic coupling – depending on both the

metal and bridging ligand. The mixed-valence species of the dirhodium species was investigated, and the electronic coupling matrix element calculated from the experimental intervalence band parameters for one of them (86 cm^{-1}) indicates a significant inter-component electronic interaction which compares well with good electron conducting anionic bridges such as cyanides. Although none of these compounds is luminescent, the M_2LCT excited state of one of the bis-dirhodium complexes is relatively long-lived (about $6\text{ }\mu\text{s}$) in degassed acetonitrile at room temperature. The results presented here are promising for the development of linear polydimetallic complexes built on longer naphthyridine-based strands, with significant long-range electronic coupling and molecular-wire-like behavior.

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Introduction

Since the discovery of mixed-valence complexes by Creutz and Taube^[1] over 30 years ago, architectures including several redox centers of the same^[2] or different^[3] nature and capable of exhibiting inter-component electronic interaction have been the center of much attention. Due to their

rich redox properties, transition metal ions connected by a bridging spacer have been the focus of much work in this field, although recent examples have also proved the tremendous potential of organic redox-active species connected through bridging transition metal complexes.^[4] A variety of systems connecting mononuclear metal ions have been explored, where the spacer is itself a ligand^[1,5] or where spacer and ligands are decoupled and involve single bonds^[6] and multiple bonds (alkynyl for 1D,^[7] 2D,^[7b,7c] and 3D^[7c] architectures; alkenyl,^[5b] cumulenes,^[7a,8] aryl^[5b,7b,7d,9a,9b]). These systems may incorporate other inert^[10a] or labile^[7b,10b] complexes and have the electronic communication between the two sites modulated by pH,^[11] light,^[12a,12b] or auxiliary ligands.^[13] The field has more recently been extended to metal–metal-bonded redox units because they themselves can include multiple bonds,^[14] similar to carbon-based units but energetically more accessible, and may therefore play the role of a conductor. The dissymmetry around the metal sites allows for testing of the communication along the metal–metal bond through axial ligands and spacers similar to their mononuclear counter-

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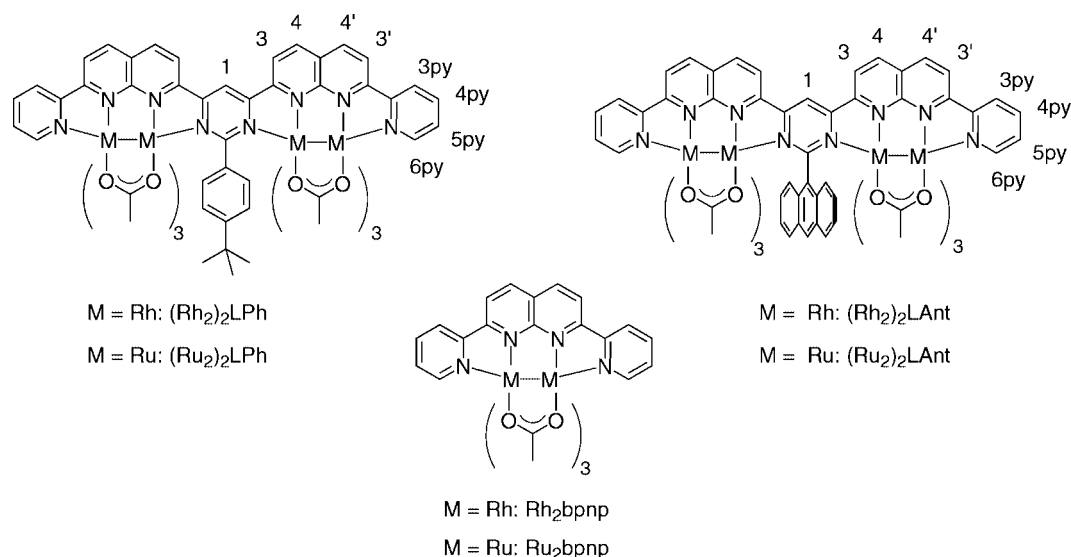


Figure 1. Formulae and abbreviation of the complexes. Numbering is related to the discussion of the ^1H NMR spectroscopic data.

parts (e.g., triple bonds^[15] and double bonds^[16]), but also successfully along the equatorial direction.^[17]

We report here the synthesis and characterization, absorption spectra, redox behavior, and spectroelectrochemistry of four bi-component systems in which each “component” or subunit is made of a metal–metal-bonded dimetallic site (Figure 1). The excited-state properties of one such species are also investigated. As we will see later, each dimetallic site can indeed be viewed as a single component of a “dinuclear” system from a redox viewpoint.

Results and Discussion

Synthesis

Ligands

The naphthyridine-based ligands 2-(4-*tert*-butylphenyl)-4,6-bis(7-pyridin-2-yl[1,8]naphthyridin-2-yl)pyrimidine (LPh) and 2-anthracen-9-yl-4,6-bis(7-pyridin-2-yl[1,8]naphthyridin-2-yl)pyrimidine (LAnt) were obtained by a Friedländer condensation methodology applied to a pyrimidine scaffold, in a very similar fashion as previously reported^[18] (Schemes 1 and 2). Two synthetic routes were used to access the central pyrimidine unit. In the case of the 4-*tert*-butylphenyl substituent leading to LPh (Scheme 1), the pyrimidine ring was built by condensation of the corresponding amidine **2**, resulting from ammonia addition to the corresponding nitrile **1**, with diethyl malonate. The obtained dihydroxypyrimidine **3** was then chlorinated with a combination of phosphoryl chloride and *N,N*-dimethylaniline to yield the dichloropyrimidine **4Ph**. The 9-anthracenyl-substituted dichloropyrimidine **4Ant**, on the other hand, was prepared directly from unsubstituted 4,6-dichloropyrimidine by deprotonation at the 2-position, reaction with 9-bromoanthracene, and oxidation with DDQ, as published earlier (Scheme 2).^[19] The dichloropyrimidines **4Ph** and **4Ant** were then coupled with 1-(tri-*n*-butylstannyl)-1-vinyl ethyl

ether^[20] and submitted to acidic hydrolysis to yield the corresponding diketones **5Ph** and **5Ant**, ready for Friedländer condensation. Once again, different routes were used for the butyl- and anthracenyl-substituted ligands. The butyl-substituted ligand was obtained by two consecutive Friedländer condensations: a base-catalyzed condensation with 4-aminopyrimidine-5-carboxaldehyde^[21] yielded pyrimidine-ended intermediate **6Ph**, which was then converted into the bis(aminocarbaldehyde) **7Ph** under acidic conditions. The latter was then condensed with commercially available 2-acetylpyridine to yield the final ligand LPh. Bis(ketone) **5Ant**, on the other hand, was directly condensed with 6-amino-2,2'-bipyridinyl-5-carbaldehyde (**9**) to yield ligand LAnt. Compound **9** was also synthesized by Friedländer condensation of 2-acetylpyridine and 4-aminopyrimidine-5-carboxaldehyde (**8**) followed by acidic hydrolysis. LAnt displays the fluorescence emission typical of anthracene derivatives.

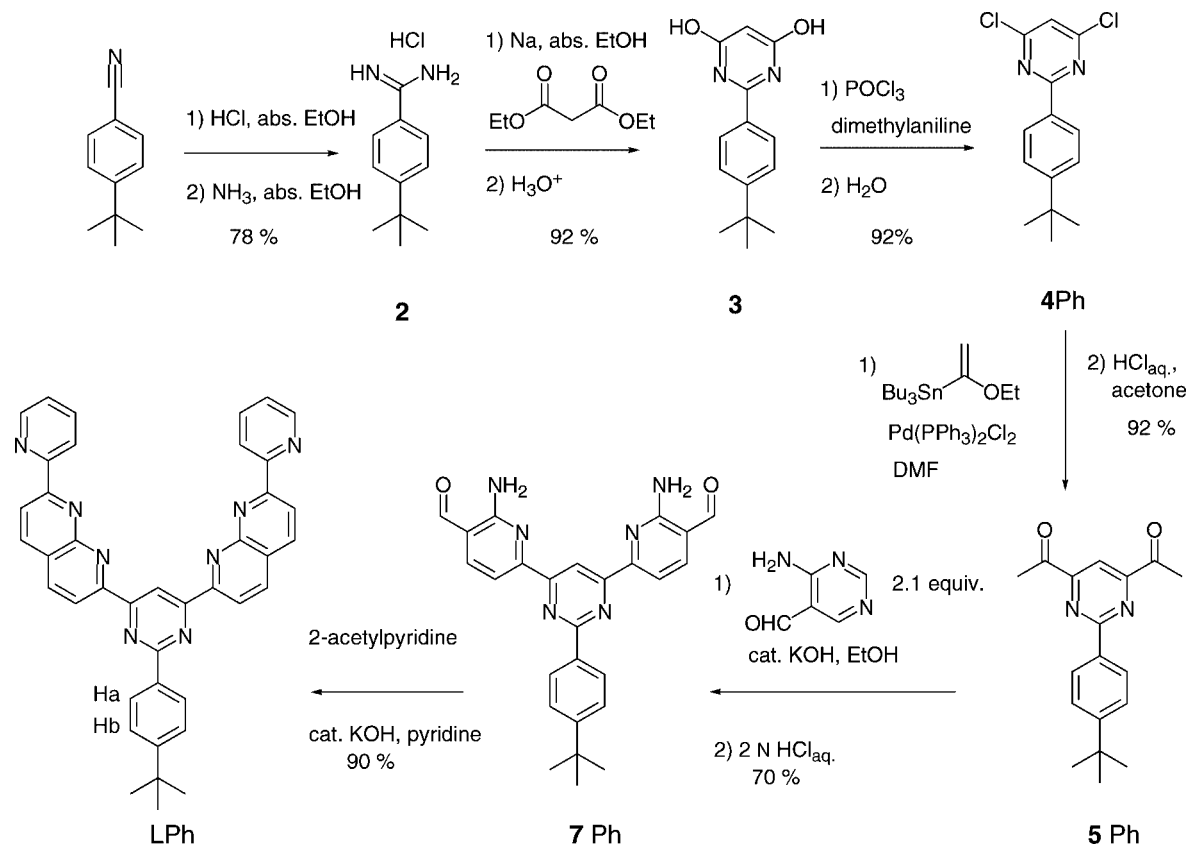
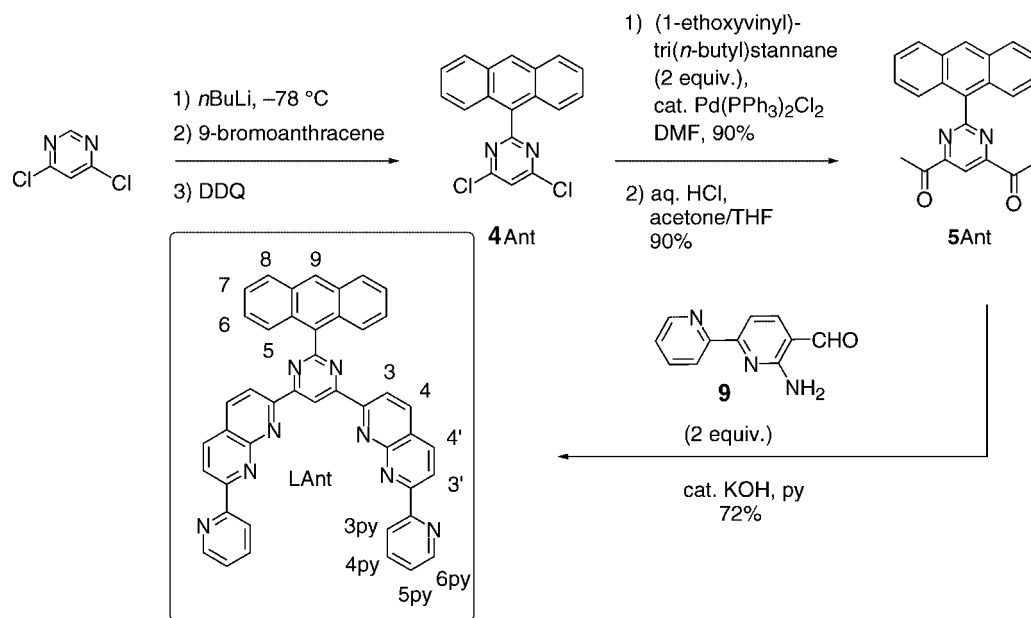
Metal Complexes

Both dirhodium complexes were obtained by treatment of a suspension of the ligand with commercially available dirhodium tetraacetate in methanol in the presence of two equivalents of protons (1 equiv. per acetate bridge to be substituted).^[22a] Heating a suspension of the ligand with the mixed-valence complex $[\text{Ru}_2(\text{OAc})_4\text{Cl}]^{[23]}$ in methanol yielded the desired diruthenium(II) complexes without additional reductant.^[22b] All complexes were isolated as their hexafluorophosphate salts.

Characterization

^1H NMR Spectroscopy

The diamagnetic dirhodium(II) complexes show a simple set of signals, thus revealing that the C_2 symmetry of the ligands is maintained in the complexes and therefore that

Scheme 1. Synthesis of LPh (numbering relates to the discussion of the ^1H NMR spectroscopic data).Scheme 2. Synthesis of LAnt (numbering relates to the discussion of the ^1H NMR spectroscopic data).

both dinuclear binding sites are occupied (in agreement with elemental analysis and mass spectrometry measurements). The two sets of signals from the acetate ligands confirm the dissymmetry introduced by a single L ligand (two different signals for the 12 equatorial and the six axial CH_3 acetate protons). The six axial acetate protons are shielded

due to the ring effect provided by the anthracene moiety, thus confirming the involvement of the pyrimidine nitrogen atoms in the coordination of the Rh_2 units and the rotation of the C–C bonds between the heteroaryl units compared to the initial ligands. Although the spectra of free ligands and metal complexes were recorded in different solvents

Table 1. Chemical shifts [ppm] of the protons in ligands LPh and LAnt (in CDCl₃) and their dirhodium complexes (in CD₃CN).

Compound	H1	H3	H3'	H3py	H4	H4'	H4py	H5py	H6py	Ha	Hb	tBu		
LPh	10.06	8.81–9.0			8.42	8.47	7.97	7.43	8.8	8.73	7.64	1.44		
[(Rh ₂) ₂ LPh]	9.71	8.8–9.0					8.58	8.29	9.67	9.24	7.75	1.49		
Compound	H1	H3	H3'	H3py	H4	H4'	H4py	H5py	H6py	H5	H6	H7	H8	H9
LAnt	10.3	8.7–8.85		9.03	8.3–8.4		7.99	7.4–7.6	8.7–8.9	7.88	7.4–7.6		8.14	8.67
[(Rh ₂) ₂ LAnt]	10.1	9.47		8.8–9.1	8.8–9.1		8.52	8.2–8.3	9.50	7.92	7.31, 7.47		8.2–8.3	8.8–9.1

and therefore the chemical shifts cannot be accurately compared (cf. *t*Bu signal as a probe of solvent effect), the introduction of the Rh₂ units has a significant deshielding effect on the protons *para* to the nitrogen atoms of the bound heterocycles (ca. +0.5 ppm for H4, H4' and H4py; Table 1) and on the pyridine protons. The substituents on the pyrimidine ring also undergo a downfield shift due to the proximity of the acetate ligands (ca. +0.5 ppm for Ha in LPh and ca. +0.2 ppm for H9 in LAnt).

The diruthenium(II) complexes are paramagnetic, as expected for the distribution of the 12 d-electrons of the two ruthenium(II) centers in a $\sigma^2\pi^4\delta^2\delta^*\pi^2$ configuration. The ¹H NMR spectra nevertheless show well-defined peaks ranging from $\delta = -50$ to 80 ppm (Figure 2) whose number is in accordance with the expected symmetry.

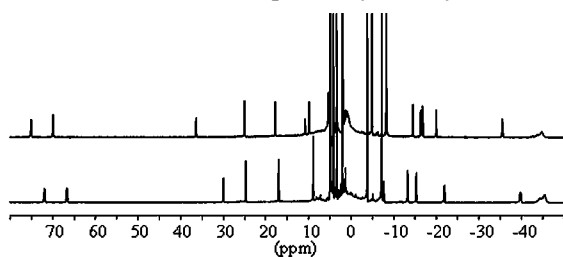


Figure 2. ¹H NMR spectra of the paramagnetic complexes [(Ru₂)₂LAnt]²⁺ (top) and [(Ru₂)₂LPh]²⁺ (bottom) (CD₃CN, 200 MHz, 25 °C).

X-ray Structure Determination

Single-crystal X-ray analysis of [(Rh₂)₂LPh]^[24] confirmed the anticipated structure of the bis-dirhodium complex (Figure 3). All nitrogen sites are bound to the rhodium centers. The distance between the two rhodium centers (2.40 Å) is the same as that found in the parent [Rh₂bnpn]⁺ complex [Rh₂ is Rh₂(OAc)₃ and bnpn is bis(pyridyl)naphthyridine],^[22a] as are the distances involving the coordinated

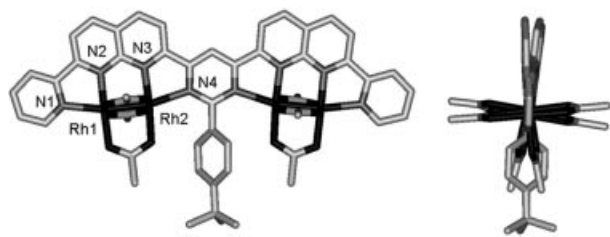


Figure 3. Solid-state structure of [(Rh₂)₂LPh]^[24] showing the alignment of the two bis-dirhodium units bridged by the central pyrimidine (hydrogen atoms, solvent, and counter anions have been omitted for clarity).

naphthyridines [Rh(1)–N(2) 2.00 and Rh(2)–N(3) 1.98 Å]. As anticipated by the difference in basicity, the strong coordinative contribution of the pyridine [Rh(1)–N(1) 2.16 Å] stands in contrast to the weaker binding of the pyrimidine ring [Rh(2)–N(4) 2.31 Å]. Overall, the quasi-planar, crescent-shaped ligand^[25] holds the two bis-dirhodium metallic units in a linear alignment that is bridged by the central pyrimidine and slightly bent by the coordination-induced pinching of the subunits.

IR Spectra

The IR spectra of all complexes show many common features (number and location of bands), which is further evidence for their similar functional and structural environments as well as identical symmetry.

Absorption Spectra

All complexes are deeply colored. The optical properties are represented in Figure 4 and reported in Table 2, together with those of the simple [M₂bnpn]⁺ dimetallic complexes reported earlier by other groups^[22a,22b] (M = Ru^{II} or Rh^{II}; these complexes were synthesized again for comparison purposes). The absorption spectra are very rich, as expected because of the presence of several chromophoric units. The spectra of all the complexes exhibit an intense absorption feature between 320 and 400 nm. This feature should therefore receive contribution from spin-allowed π – π^* transitions involving the common L bridging ligand. In [(Rh₂)₂LAnt] and [(Ru₂)₂LAnt], the spin-allowed, anthracene-centered ¹L_a transitions are expected within the same wavelength range,^[26c,27,28] and their contribution is clear when looking at the vibrational progression appearing in the spectra of both species. For these latter species, the very intense absorption band around 254 nm can be straightforwardly assigned to the ¹B_a transition of the anthryl subunits.^[26c,27,28]

As far as the visible absorption is concerned, the lowest-energy band of the rhodium species is attributed to a charge-transfer transition from each dirhodium subunit (most likely from a π^* orbital extending over the two metal centers) to the bridging ligand. Such a transition is a form of metal–metal to ligand charge transfer (M₂LCT) transition because of the strong interaction between the metal–metal-bonded units of each component. The red shift of the lowest-energy absorption band in the present compounds { $\lambda_{\text{max}} = 622$ and 634 nm for [(Rh₂)₂LPh] and [(Rh₂)₂LAnt], respectively} compared to that of the parent species [Rh₂bnpn] ($\lambda_{\text{max}} = 578$ nm) supports the CT assignment, since in the dicomponent species the LUMO of the polypyridine

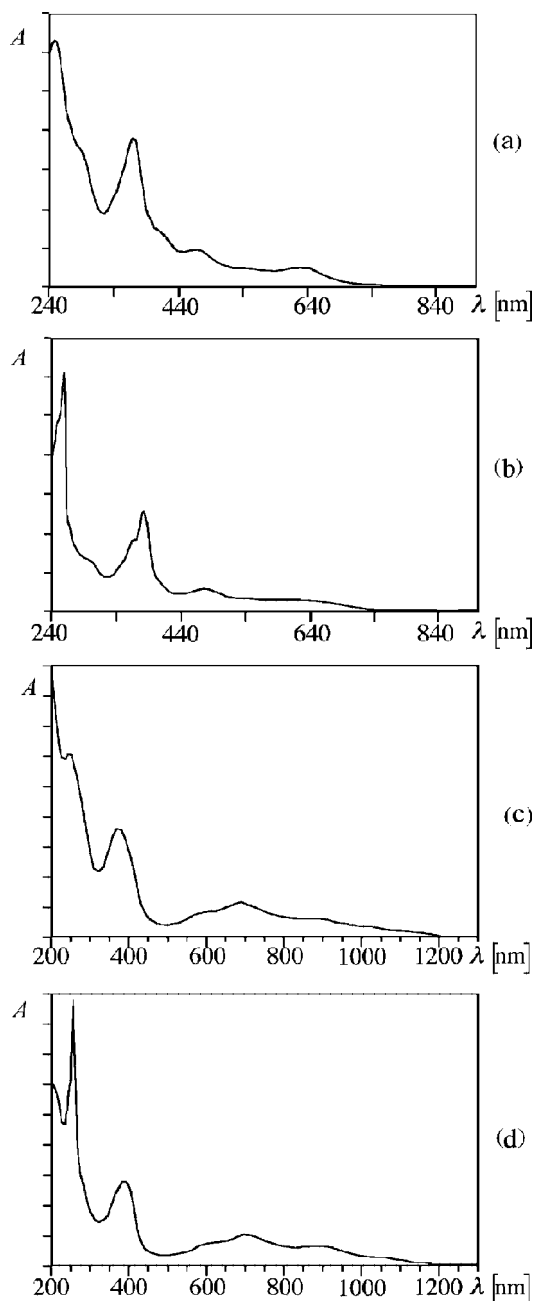


Figure 4. Absorption spectra of $[(\text{Rh}_2)\text{LPh}(\text{Rh}_2)]$ (a), $[(\text{Rh}_2)\text{LAnt}(\text{Rh}_2)]$ (b), $[(\text{Ru}_2)\text{LPh}(\text{Ru}_2)]$ (c), and $[(\text{Ru}_2)\text{LAnt}(\text{Ru}_2)]$ (d) in acetonitrile solution.

Table 2. Absorption data in CH_3CN at room temperature.

	λ_{max} [nm] ($\log_{10} \epsilon$ [$\text{M}^{-1} \text{cm}^{-1}$])							
$[\text{Rh}_2\text{bpnp}]\cdot\text{PF}_6$	248 (4.69)	283 (4.33)	346 (4.46)	363 (4.63)	408 sh (3.34)	440 sh (3.08)	540 sh (3.40)	578 (3.52)
$[(\text{Rh}_2)\text{LPh}(\text{Rh}_2)]\cdot 2\text{PF}_6$	250 (4.9)	292 (4.6)	347 sh (4.5)	371 (4.6)	412 sh (4.2)	468 (4.0)	543 (3.7)	622 (3.7)
$[(\text{Rh}_2)\text{Ant}(\text{Rh}_2)]\cdot 2\text{PF}_6$	248 (3.1)	254 (5.2)	295 (4.5)	347 sh (4.5)	364 (4.6)	382 (4.8)	478 (4.1)	545 (3.8)
$[\text{Ru}_2\text{bpnp}]\cdot\text{PF}_6$	246 (4.5)	274 (4.4)	287 (4.3)	351 (4.5)		440 sh (3.35)	520 sh (3.4)	586 sh (3.6)
$[(\text{Ru}_2)\text{LPh}(\text{Ru}_2)]\cdot 2\text{PF}_6$	248 (4.8)	270 sh (4.6)		370 (4.6)		400 sh (4.4)	600 (4.0)	695 (4.2)
$[(\text{Ru}_2)\text{LAnt}(\text{Ru}_2)]\cdot 2\text{PF}_6$	254 (4.7)			369 (4.5)		387 (4.6)	602 (4.0)	701 (4.2)

idine-type bridging ligand (i.e., the acceptor orbital of the CT transition) is lower in energy than the LUMO of bpnp (see below).

For the ruthenium compounds, the absorption bands, which have a similar origin to those of the rhodium analogues, are displaced to lower energies than the rhodium species, with the lowest-energy band in the near-IR region (Figure 4). This is also in agreement with a M_2LCT assignment, since the metal-based HOMOs of the ruthenium compounds are higher in energy than those of the corresponding rhodium species (see redox behavior).

Redox Behavior

The four bis-dimetallic species investigated here exhibit a rich redox behavior. Figure 5 shows the cyclic voltammograms of the compounds and Table 3 reports the main redox data, together with data relative to the free ligands (bpnp and LPh) and parent $[\text{Rh}_2\text{bpnp}]^+$ complex for comparison. To better evidence the bi-component nature of the studied compounds, these latter are labeled $(\text{M}_2)_2\text{L}(\text{M}_2)$ instead of $(\text{M}_2)_2\text{L}$ ($\text{M} = \text{Rh}$ or Ru ; $\text{L} = \text{LPh}$ or LAnt) in this paragraph.

As already discussed,^[24] the easier reduction of the LPh ligand compared to the bpnp ligand ($\Delta E_{1/2}^{\text{first-red}} = -0.28$ V) is mirrored by the reduction properties of the complexes, with $[(\text{Rh}_2)\text{LPh}(\text{Rh}_2)]$ being easier to reduce than $[\text{Rh}_2\text{bpnp}]^+$ ($\Delta E_{1/2}^{\text{first-red}} = -0.43$ V). This observation is in accordance with earlier work describing the LUMO of $[\text{Rh}_2(\text{acetate})_3\text{L}]^+$ complexes ($\text{L} =$ chelating pyridine/naphthyridine-type ligand) as being mainly ligand-based.^[29] Substituting a pyridine for a more easily reduced pyrimidine yields a new ligand and its derived complexes with less negative reduction potentials. The lowering of the LUMO of polypyridyl-type ligands upon complexation has also already been observed.^[26b] Such considerations allow us to assign the reduction potential of all the bis-dimetallic complexes studied here to bridging-ligand-based processes.

Table 3 also indicates that both bis-dirhodium complexes are easier to reduce than their bis-diruthenium counterparts (ca. 0.1 V difference). This may be due to an enhanced π back-donation in the bis-diruthenium complexes, which have metal-centered HOMOs of higher energy (see below).

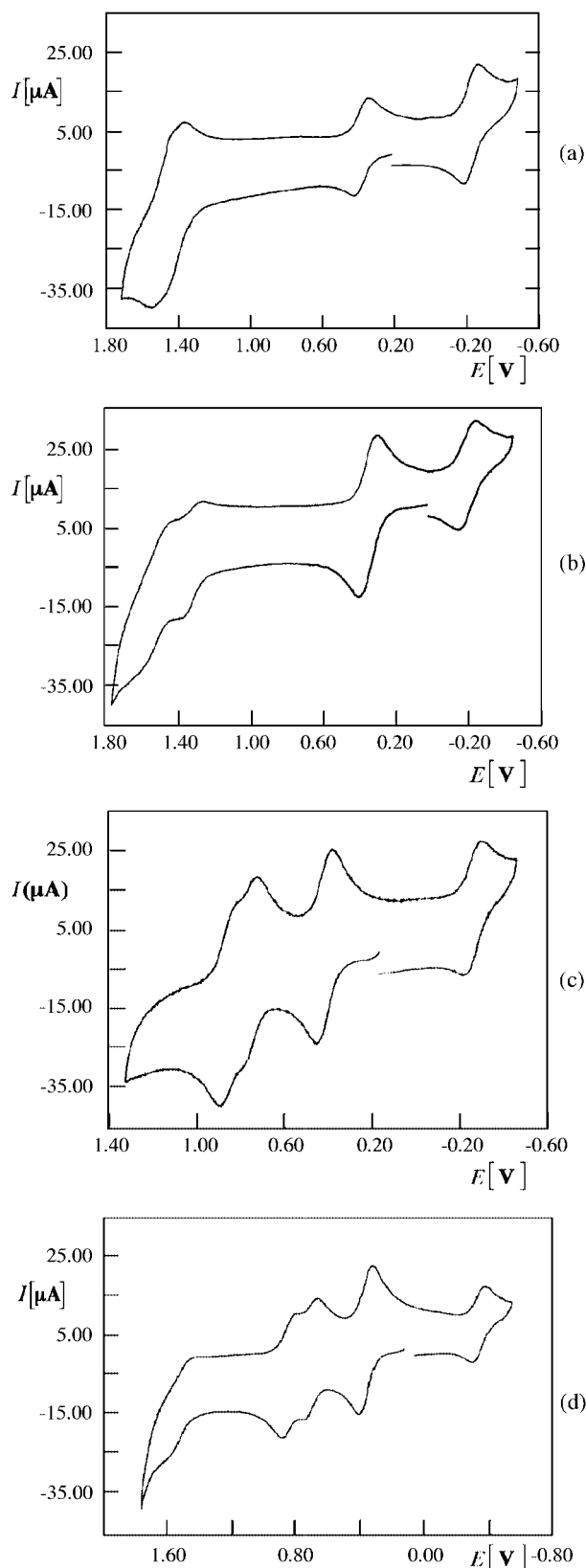


Figure 5. Cyclic voltammograms (vs. SCE) of the four complexes $[(\text{Rh}_2)\text{LPh}(\text{Rh}_2)]$ (a), $[(\text{Rh}_2)\text{LAnt}(\text{Rh}_2)]$ (b), $[(\text{Ru}_2)\text{LPh}(\text{Ru}_2)]$ (c), and $[(\text{Ru}_2)\text{LAnt}(\text{Ru}_2)]$ (d) in acetonitrile at room temperature. Scanning rate: 500 mV s^{-1} . The process at about 0.4 V is the ferrocene oxidation, used as an internal reference.

Table 3. Half-wave potentials (vs. SCE) for the oxidation and first reduction of the four bis-dimetallic complexes and of reference species in acetonitrile at room temperature (0.5 mM , 0.05 M $\text{NBu}_4\text{-ClO}_4$). Number of exchanged electrons in square brackets. The processes are reversible unless otherwise stated.

Compound	Oxidation, $E_{1/2}$ [V] vs. SCE	Reduction, $E_{1/2}$ [V] vs. SCE
bnp ^[a]	no oxidation at $V < +1.80$	-1.64 [1]
LPh ^[a]	no oxidation at $V < +1.80$	-1.36 [1]
$[\text{Rh}_2\text{bnp}]^{\text{[a]}}$	$+1.30$ [1]	-0.64 [1]
$[(\text{Rh}_2)\text{LPh}(\text{Rh}_2)]$	$+1.43$ [1], $+1.50$ [1]	-0.21 [1] ^[b]
$[(\text{Rh}_2)\text{LAnt}(\text{Rh}_2)]$	$+1.32$ [1], $+1.53$ [2] ^[c]	-0.18 [1] ^[b]
$[(\text{Ru}_2)\text{LPh}(\text{Ru}_2)]$	$+0.76$ [1], $+0.85$ [1]	-0.31 [1] ^[b]
$[(\text{Ru}_2)\text{LAnt}(\text{Ru}_2)]$	$+0.73$ [1], $+0.86$ [1], $+1.51$ [1] ^[c]	-0.30 [1] ^[b]

[a] Data taken from ref.^[24] For the free ligands, the solvent is dichloromethane and the reported values were obtained at 0°C . [b] Further reduction processes take place for all the complexes but they are ill-behaved and will not be discussed here. [c] Irreversible process.

The contribution of the diruthenium unit to the LUMO destabilization thus results in a more negative reduction potential.

Several oxidation waves are observed for all complexes, as evidenced by the cyclic voltammograms reported in Figure 5. $[(\text{Rh}_2)\text{LPh}(\text{Rh}_2)]$ shows two very close oxidation waves (resolved by differential voltammetry), each of which corresponds to a one-electron oxidation and is related to the sequential removal of one electron from each Rh_2 unit. Therefore, the first oxidation process leads to the mixed-valence, bi-component system $[(\text{Rh}_2^{5+})\text{LPh}(\text{Rh}_2^{4+})]$, whereas $[(\text{Rh}_2^{5+})\text{LPh}(\text{Rh}_2^{5+})]$ is obtained upon further oxidation. The first one-electron oxidation of $[(\text{Rh}_2)\text{LAnt}(\text{Rh}_2)]$ is followed by a two-electron irreversible oxidation at 1.53 V . To assign the various processes occurring in this latter compound to specific subunits, it is useful to consider that an irreversible oxidation at $+1.51 \text{ V}$ is observed for $[(\text{Ru}_2)\text{LAnt}(\text{Ru}_2)]$ (attributed to oxidation of the anthryl center, see below) and the second oxidation of the dimetallic subunit of $[(\text{Rh}_2)\text{LPh}(\text{Rh}_2)]$ occurs at $+1.50 \text{ V}$ (see above). It is therefore likely that the first oxidation process of $[(\text{Rh}_2)\text{LAnt}(\text{Rh}_2)]$ corresponds to the oxidation of one bimetallic subunit and the subsequent irreversible bi-electronic oxidation involves both the one-electron oxidation of the second Rh_2 unit and the irreversible oxidation of the anthracene unit.

Both the bis-diruthenium complexes are much easier to oxidize than their bis-dirhodium counterparts. This indicates that the HOMOs are higher in energy for the diruthenium centers than for the dirhodium ones. Once again, two consecutive one-electron oxidations occur for the bis-ruthenium species (Table 3, Figure 5), which are assigned to the consecutive oxidation of the interacting dimetallic subunits. The additional irreversible oxidation at 1.51 V in $[(\text{Ru}_2)\text{LAnt}(\text{Ru}_2)]$, mentioned above, is attributed to the anthracene oxidation.

Intercomponent Interactions

The observation of two distinct oxidation potentials for the two M_2 units in $[(\text{M}_2)\text{LPh}(\text{M}_2)]$ and $[(\text{M}_2)\text{LAnt}(\text{M}_2)]$

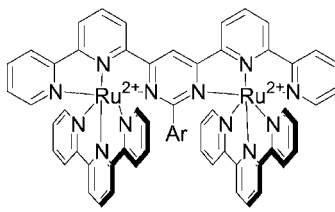
suggests that a non-negligible electronic interaction exists between the two metal–metal-bonded dimetallic subunits of the four complexes. Actually, the difference between the two oxidation potentials is a function of the degree of interaction between the two redox centers.^[30] The splittings between the first two oxidation waves reported in Table 4 show that [(Ru₂)LPh(Ru₂)] displays a slightly greater degree of electronic interaction than its bis-dirhodium counterpart (for the LAnt series, overlap between the second metal-based oxidation and the anthracene-based irreversible oxidation in [(Rh₂)LAnt(Rh₂)] makes the comparison meaningless). To rationalize such a difference, it is useful to recall that, beside Coulombic factors, which are expected to be identical for both the dirhodium and diruthenium compounds studied here, contribution to the electronic interaction can be related to the separation between the energetic levels of the HOMOs, which are centered on the metallic unit, and the LUMO, which is centered on the bridging ligand, assuming that an effective mechanism for inter-component electronic interaction is superexchange via an electron-transfer pathway involving the bridging ligands.^[30] Hence, on the basis of the Koopman theorem, which approximates the energy of the orbitals to the redox potential values, a smaller difference between first oxidation and reduction potentials corresponds to a larger inter-component interaction. From the redox data in Table 3, the HOMOs of the bis-diruthenium compounds are located at higher energy than those of the bis-dirhodium species, and this justifies why the interaction is larger in the former compounds (the effect on the HOMO is only partially compensated by a reversed effect on the LUMO).

As highlighted in Table 4, it also appears that the anthracene-derived ligand promotes a larger electronic coupling than the 4-*tert*-butylphenyl-substituted ligand: the half-potential difference for [(Ru₂)LAnt(Ru₂)] is 0.13 V, compared with 0.09 V for [(Ru₂)LPh(Ru₂)], and, although the potential of the metal-based oxidation of [(Rh₂)LAnt(Rh₂)] is not known exactly, the same appears also to be valid for the dirhodium couple of complexes. Comparison between the

redox properties of the bis-dimetallic compounds studied here with those of closely related dinuclear complexes in which each component is made by a Ru^{II} polypyridine subunit^[26b–26d] reveals striking similarities. The structure of the naphthyridine-based ligands LPh and LAnt is indeed derived from that of the pyridine-based parents L'Ph and L'Ant, which accommodate mononuclear ruthenium(II) complexes (see Table 4, right, for the structure of the Ru^{II} complexes). Interestingly, the enhancement of the electronic interaction provided by the anthracene pyrimidine substituent in the bis-dimetallic complexes and the “classic” dinuclear Ru^{II} polypyridine complexes^[26b–26d] is the same (0.04 V), thus suggesting that similar processes could be occurring.

Two main contributions can explain the anthracene effect. On the one hand, the anthracene moiety moves the electronic levels of the bridging ligand to lower energies, as also suggested by the reduction potentials {[(Rh₂)LAnt(Rh₂)] is easier to reduce than [(Rh₂)LPh(Rh₂)], see Table 3, with the reduction mainly based on the bridging ligand}, probably because the anthryl substituent can contribute to a better delocalization of the added electron. As a consequence, the LUMO–HOMO gap becomes smaller and the interaction is enhanced. However, according to this mechanism, the effect on the HOMO(s) should be negligible, but this is not the case, since the data in Table 3 indicate that on passing from the LPh to the LAnt series the HOMOs are even more affected than the LUMO by the presence of the anthracene group. On the other hand, the anthracene moiety may contribute to the electronic coupling between the redox sites by opening a new pathway for superexchange, for example by mediating a through-space interaction involving anthracene-based orbitals. The redox data indeed indicate that the anthracene-based HOMO is close in energy to the metal-centered orbitals, so that a hole-transfer pathway involving the anthracene HOMO is quite possible. It is likely that both contributions come into play. This situation is schematized in Figure 6.

Table 4. Differences in half-wave potentials between the first two one-electron oxidations of the four bis-dimetallic complexes and the two related ruthenium-based bis-mononuclear analogues (the structure of the latter is presented on the right).

Complex	$E_{1/2}^{\text{ox}2} - E_{1/2}^{\text{ox}1}$		
(Rh ₂)LPh(Rh ₂)	0.07 V ^[a]		
(Rh ₂)LAnt(Rh ₂)	n.d. ^[b]		
(Ru ₂)LPh(Ru ₂)	0.09 V ^[a]		
(Ru ₂) ₂ LAnt(Ru ₂)	0.13 V ^[a]		
(Ru)L'Ph(Ru)·4 PF ₆	0.13 V ^[c]	(Ru)L'Ph(Ru)·4 PF ₆	Ar = Ph
(Ru)L'Ant(Ru)·4 PF ₆	0.17 V ^[c]	(Ru)L'Ant(Ru)·4 PF ₆	Ar = 9-Ant

[a] In acetonitrile. [b] Not determined due to overlap of the second oxidation signal with the anthracene peak. [c] DMF.

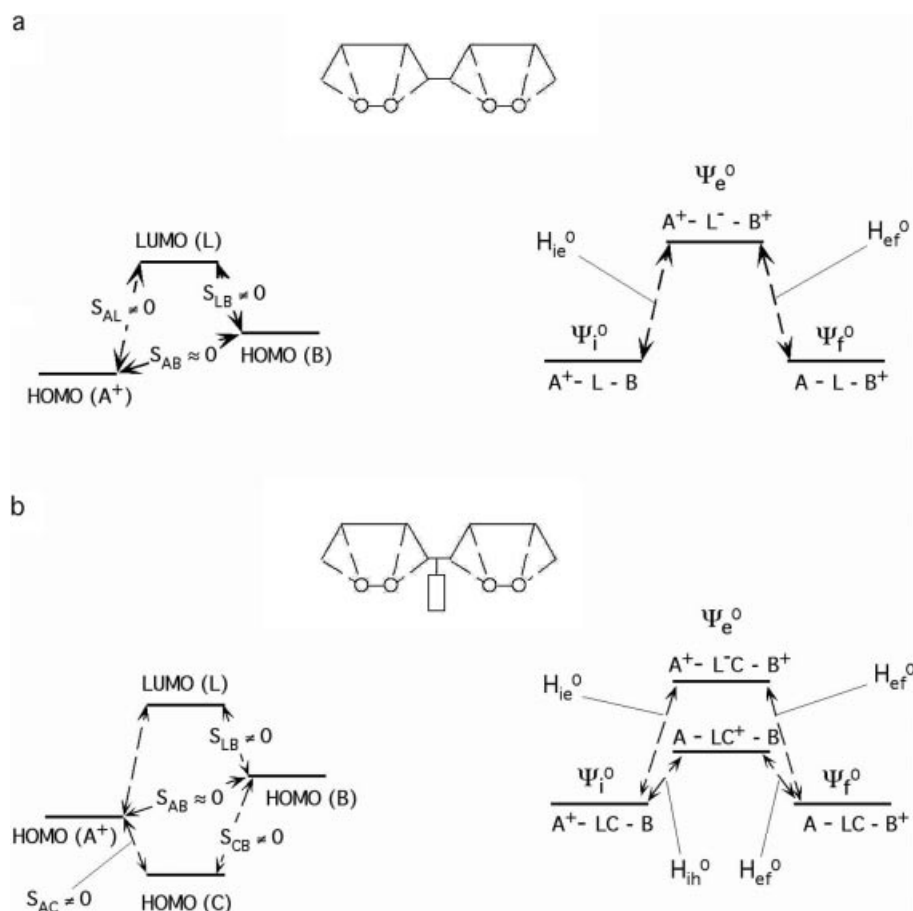
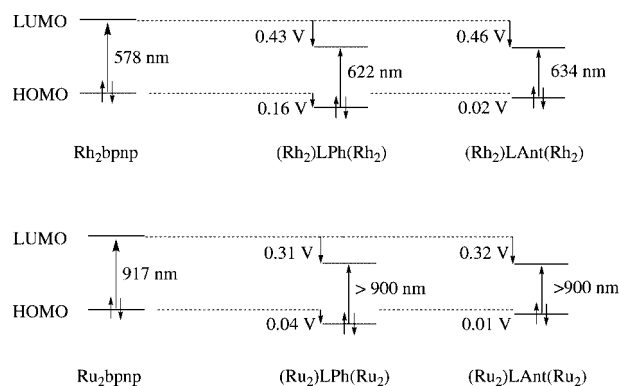


Figure 6. Schematic representation of the interaction between the subunits. In the scheme, A and B represent the dimetallic subunits, with one of them oxidized (so the mixed-valence species is considered, for clarity). (a) refers to species with LPh as the bridge and (b) to LAnt as the bridging ligand. Orbital interactions are shown on the left and interactions between states are represented on the right. In (b), the anthracene (identified as “C”) HOMO contributes to the overall coupling; the bridge is here labeled LC on the “state” diagram to highlight the contribution of anthracene. S indicates overlap integrals, Ψ the wavefunctions of the various states, and H the electron coupling matrix elements. The superscript 0 indicates zero-order quantities (i.e. quantities that derive from pure, localized electronic configurations). The subscripts i, f, e, and h indicate the initial, final, electron- and hole-transfer states, respectively (these latter two are “virtual” states).^[30]

The electronic information gathered through the electrochemical (and electronic absorption) studies reported above is summarized in Scheme 3. In both the metal–metal-bonded dirhodium and diruthenium complexes, the LUMO–HOMO gap is reduced on going from the bnp-



Scheme 3. Compared electronic levels of the one and two dimetallic site complexes of rhodium and ruthenium.

based “mononuclear” to the LPh- and LAnt-based “dinuclear” complexes, mainly due to a significant LUMO lowering (LUMO centered on the ligand where a pyridine is substituted by a pyrimidine, plus bimetallic coordination of the second chelating site). An additional gap reduction is caused by changing the substitution of the pyrimidine substituent from a phenyl to an anthryl moiety, which results in a small further decrease of the LUMO energy and an increase of the HOMO level.

Spectroelectrochemistry

The splitting of the oxidation processes of the four bis-dimetallic compounds, which indicates a relatively high stability of the mixed-valence species with respect to the iso-valent forms,^[31] prompted us to investigate the properties of their mixed-valence compounds in more detail by performing spectroelectrochemistry experiments. However, results were poor for the ruthenium complexes: featureless absorption spectra were obtained, probably due to the very

broad and unresolved absorption spectra of the starting compounds (see Figure 4), particularly in the otherwise diagnostic visible and near-IR region. For this reason, our discussion will be limited to $[(\text{Rh}_2)\text{LPh}(\text{Rh}_2)]$ and $[(\text{Rh}_2)\text{LAnt}(\text{Rh}_2)]$.

Figure 7 shows the changes in the absorption spectrum of $[(\text{Rh}_2)\text{LPh}(\text{Rh}_2)]$ on applying increasingly positive potentials. At the beginning (potential: +1.45 V), a slight increase of absorption in the range 680–900 nm occurs, with simultaneous decrease of the absorption of the M_2LCT band at about 640 nm. A slight absorption decrease of the 350-nm band also takes place, with formation of a new absorption in the range 380–450 nm. The absorption feature in the red is attributed to an intervalence transfer (IT) transition from the Rh_2^{4+} subunit to the Rh_2^{5+} component of the mixed-valence “dinuclear” $[(\text{Rh}_2^{5+})\text{LPh}(\text{Rh}_2^{4+})]$ species obtained upon first oxidation, whereas the decrease of the M_2LCT band is a consequence of the disappearance of one of the donor orbitals of the corresponding CT transition. The changes in the 340–440-nm region are probably the consequence of an asymmetry of the coordination sites of the otherwise symmetric bridge induced by the mixed-valence nature of the species. On increasing the applied potential, a new process starts, as indicated by the isosbestic points at about 440 and 345 nm (not visible in Figure 7, where only a limited numbers of spectra are shown for clarity): the IT band disappears, as does the M_2LCT band, and the ligand-centered bands continue to change. The final spectrum is constant upon successive increase of applied potential, and the initial spectrum is recovered when the potential is eliminated, in agreement with the reversibility of the oxidation processes.

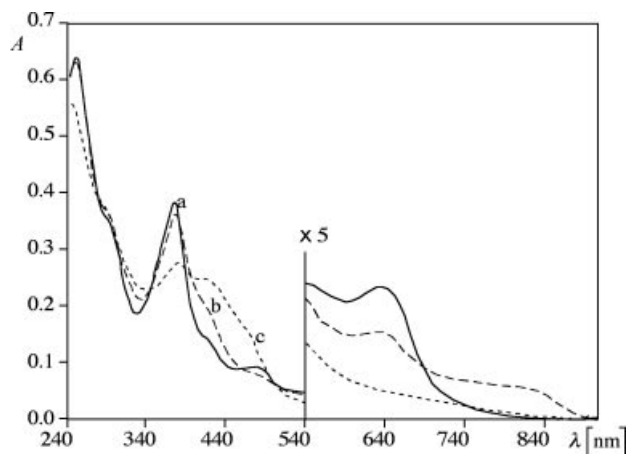


Figure 7. Changes in the absorption spectrum of $[(\text{Rh}_2)\text{LPh}(\text{Rh}_2)]$ in acetonitrile on applying positive potentials: (a) starting spectrum; (b) applied voltage of +1.45 V; (c) applied voltage of +1.60 V.

Figure 8 shows the changes of the absorption spectrum of $[(\text{Rh}_2)\text{LAnt}(\text{Rh}_2)]$ upon oxidation at relatively mild potentials. In this case, probably due to the increased separation between the two oxidation potentials (Table 4), it is possible to follow the first oxidation process in more detail, as evidenced by the several isosbestic (or quasi-isosbestic) points. Indeed, Figure 8 only shows changes related to the

first oxidation process: as for the former compound, a new absorption (assigned to the IT transition) appears in the 680–900-nm region even for $[(\text{Rh}_2)\text{LAnt}(\text{Rh}_2)]$, with concomitant decrease of the M_2LCT band and changes in the 330–450-nm ligand-centered region. Removing the applied potential leads back to the starting spectrum quantitatively, whereas the increase of the positive applied potential leads to the disappearance of both IT and M_2LCT bands and further changes in the ligand-centered region (not shown) also in this case.

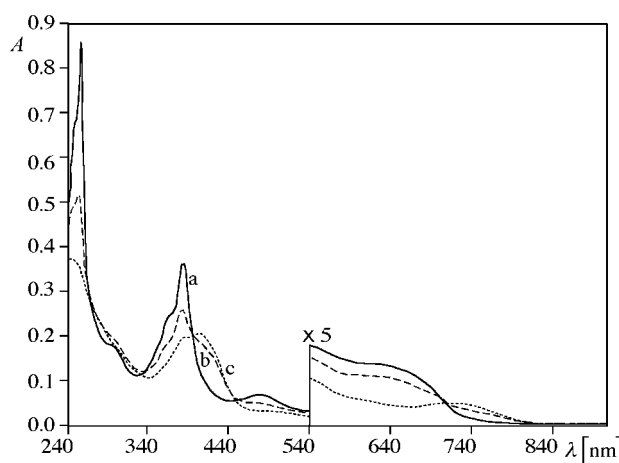


Figure 8. Changes in the absorption spectrum of $[(\text{Rh}_2)\text{LAnt}(\text{Rh}_2)]$ in acetonitrile on applying positive potentials: (a) starting spectrum; (b) applied voltage of +1.40 V; (c) applied voltage of +1.55 V.

The possibility of following the formation and disappearance of the IT band in $[(\text{Rh}_2)\text{LAnt}(\text{Rh}_2)]$ allowed us to calculate the electronic interaction parameters from Equation (1).^[32]

$$\epsilon_{\text{max}} = (2380 \, r^2 / E_{\text{op}} \, \Delta\nu^{1/2}) \, H_{\text{AB}}^2 \quad (1)$$

According to Hush,^[32] Equation (1) correlates the optical inter-valence transfer band with the magnitude of the electronic coupling matrix element between the two subunits A and B (in the present case, the Ru_2^{4+} subunits), H_{AB} , ϵ_{max} is the maximum molar absorption coefficient of the IT band, E_{op} and $\Delta\nu$ are the band maximum energy and half-width (in cm^{-1}), respectively, and r is the inter-component distance (in Å). For $[(\text{Rh}_2)\text{LAnt}(\text{Rh}_2)]$, ϵ_{max} is $1900 \, \text{M}^{-1} \text{cm}^{-1}$, E_{op} is $13700 \, \text{cm}^{-1}$, $\Delta\nu$ is $3000 \, \text{cm}^{-1}$, and r is $9.0 \, \text{Å}$ (r is taken as the center-to-center distance). By using the above experimental parameters, a value of $86 \, \text{cm}^{-1}$ is calculated for H_{AB} . This value compares well with the electronic coupling matrix elements of dinuclear Ru^{II} polypyridine complexes bridged by good electron coupling mediator spacers such as cyanide ligands,^[33] thus confirming the significant inter-component interaction mediated by the LAnt bridge.

Excited-State Properties

None of the four bis-dimetallic compounds studied here (including the two species containing the LAnt ligand,

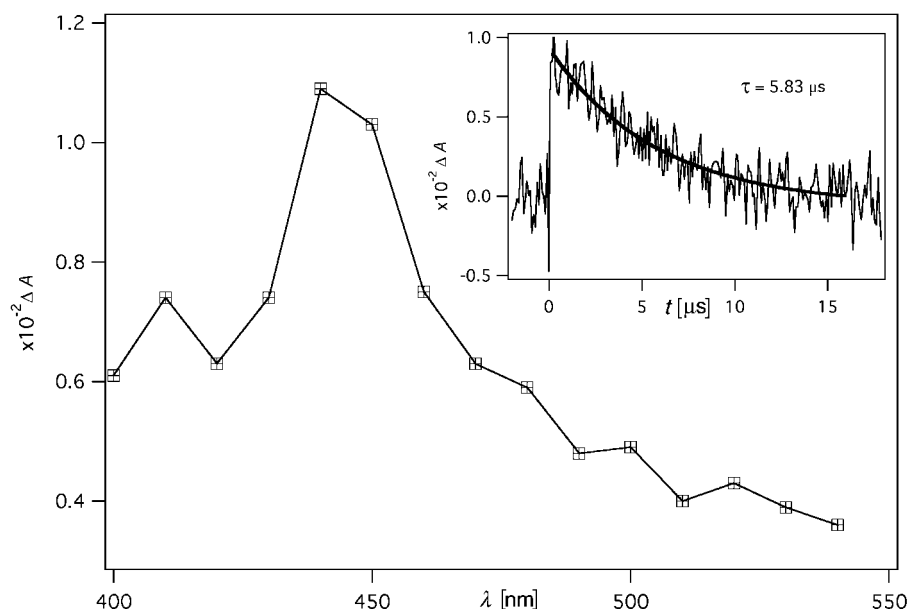


Figure 9. Transient absorption spectrum and (inset) decay of $[(\text{Rh}_2)\text{LPh}(\text{Rh}_2)]$ in acetonitrile. Excitation wavelength: 532 nm.

which shows the typical anthracene fluorescence when not coordinated to metals) exhibits any luminescence, either at room temperature or at 77 K. This agrees with the excited-state properties of metal–metal-bonded acetate species, which are known to deactivate by nonradiative transitions.^[34] However, it has recently been reported^[35] that dirhodium compounds of this class, although nonluminescent, can exhibit lifetimes on the microsecond timescale and can therefore be easily involved in bimolecular photoinduced electron- and energy-transfer processes. This is the case, for example, for the complexes $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{L})_2]$ ($\text{L} = \text{CH}_3\text{OH}$, tetrahydrofuran, triphenylphosphane, pyridine).^[35] However, the nature of the long-lived excited state was not clarified.

The similarity between the dirhodium complexes reported to exhibit the long-lived excited state^[35] and the bisdimetallic species studied here prompted us to perform nanosecond transient absorption spectroscopy (in degassed acetonitrile at room temperature) on the present systems. With our nanosecond-limited equipment, no transient spectrum could be recorded for $[(\text{Rh}_2)\text{LAnt}(\text{Rh}_2)]$, $[(\text{Ru}_2)\text{LAnt}(\text{Ru}_2)]$, or $[(\text{Ru}_2)\text{LPh}(\text{Ru}_2)]$. This suggests that the excited states of these latter species decay faster than the laser flash (10 ns). On the contrary, a clear absorption feature appeared in the transient absorption spectrum of $[(\text{Rh}_2)\text{LPh}(\text{Rh}_2)]$. This transient absorption exhibits a broad maximum around 440 nm that extends over a large part of the visible region (Figure 9). It resembles the absorption spectrum of the *reduced* $[(\text{Rh}_2)\text{LPh}(\text{Rh}_2)]$, so it can be assigned to the absorption of the radical anion of the bridging ligand, in agreement with the M_2LCT assignment of the lowest-energy excited state for the complex.

The transient spectrum of $[(\text{Rh}_2)\text{LPh}(\text{Rh}_2)]$ disappears with a monoexponential decay, yielding a lifetime of 5.8 μs , the same timescale reported for the excited state of other

metal–metal-bonded dirhodium complexes.^[35] The reason for the absence of such long excited-state lifetimes in the other compounds studied here could be the nature of the metal (for the diruthenium species, for which the M_2LCT state is probably so low in energy that nonradiative transitions are very fast) and the presence of the anthracene moiety {for $[(\text{Rh}_2)\text{LAnt}(\text{Rh}_2)]$; the anthracene moiety could introduce other low-lying excited states, such as an anthracene-to-bridging ligand CT level, which can accelerate the decay to the ground state}. Nevertheless, the relatively long-lived excited state of $[(\text{Rh}_2)\text{LPh}(\text{Rh}_2)]$ indicates that this class of compounds also has a good potential to be involved in processes based on light as the energy input.

Conclusion

The naphthyridine-based ligands reported here are able to accommodate two sets of dimetallic redox active units that show electronic communication with one another. Bisdirhodium and bisdiruthenium complexes of similar structure have been synthesized and characterized. Among the two families of species, electronic communication is stronger in the diruthenium complexes than in their dirhodium counterparts and is further enhanced by the replacement of the phenyl group born by the bridging pyrimidine with an anthryl moiety. The positive effect of the anthracene substituent on the electronic communication between dimetallic units is similar to that observed earlier with analogous mononuclear ruthenium complexes and is proposed to be mainly due to the involvement of an anthracene-based HOMO in the interaction mechanism. Moreover, one of the compounds exhibits a long-lived (microsecond timescale) excited state. The results presented here are promising for the development of poly-dimetallic complexes built on

longer naphthyridine-based strands. Furthermore, the replacement of the bridging pyrimidine by a pyrazine group should lead to a linear (not curved) structure with stronger electronic coupling between subunits, as is the case in mononuclear bi-component complexes.^[26e] The introduction of dimetallic units characterized by single metal–metal (such as the those described here) but also by multiple metal–metal bonds (e.g., Mo₂, Re₂) in larger ligands is currently in progress to extend the work on mononuclear ruthenium racks^[26] towards nanoscale molecular wires.^[36]

Experimental Section

Materials and Methods: All reagents were used as received. Dry solvents (dichloromethane, toluene, THF) were distilled over drying agents (calcium hydride, Na, Na/benzophenone, respectively) under argon. 4-Amino-5-cyanopyrimidine,^[37] 4-aminopyrimidine-5-carboxaldehyde,^[21] (1-ethoxyvinyl)tri(*n*-butyl)stannane,^[20] 2-(anthracen-9-yl)-4,6-dichloropyrimidine,^[26b] and tetra- μ -acetodiruthenium(II,III) chloride [Ru₂(OAc)₄Cl]^[23] were prepared according to published protocols. ¹H and ¹³C NMR spectra were recorded with a Bruker AC 200 (200 and 50 MHz respectively) at 25 °C. Electronic and luminescence spectra were recorded with a Varian CARY 13e and an AMINCO Bowman Series 2 spectrometer, respectively, in the reported spectroscopic grade solvents. Mass spectrometry was performed at the Laboratoire de Spectrométrie de masse Bio-organique (LSMBO, Strasbourg, France) and elemental analyses at the elemental analysis service, Louis Pasteur University (Strasbourg, France). IR spectra: (f) = weak, (F) = strong, (m) = medium.

The electrochemical equipment and methods have been described previously.^[26e] Absorption spectroscopy in the near-IR region were recorded with a JASCO V570 spectrophotometer. For spectroelectrochemical measurements, the latter spectrophotometer was used in connection with an EG&G 273A potentiostat. Nanosecond transient absorption experiments were performed in argon-purged acetonitrile solutions. A Continuum Surelite SLI-10 Nd:YAG laser was used to excite the sample with 10-ns pulses at 355 nm. The monitoring beam was supplied by a Xe arc lamp, and the signal was detected by a red-sensitive photodiode after passing through a high radiance monochromator. Differential absorption spectra were recorded point-by-point, while kinetic measurements were made at a fixed wavelength. Sixty four individual laser shots were averaged to improve the reliability of each acquisition. The signals were stored and analyzed on a dedicated PC.

7-(Pyridin-2-yl)pyrido[2,3-*d*]pyrimidine (8): Two drops of 10% methanolic sodium hydroxide were added to a hot solution of 4-aminopyrimidine-5-carboxaldehyde^[21] (198 mg, 1.61 mmol) and 2-acetylpyridine (220 mg, 1.82 mmol, 1.13 equiv.) in 23 mL of absolute ethanol. The solution was then refluxed for 4 h under argon and concentrated in vacuo. The residue was recrystallized from ethanol to yield 229 mg of an off-white solid (68%, m.p. 205 °C). ¹H NMR (CDCl₃): δ = 9.57 (s, 1 H), 9.50 (s, 1 H), 8.92 (d, ³*J* = 8.5 Hz, 1 H), 8.88 (d, ³*J* = 7.9 Hz, 1 H), 8.8 (br. d, 1 H), 8.44 (d, ³*J* = 8.5 Hz, 1 H), 7.93 (td, ³*J* = 7.9, ⁴*J* = 1.7 Hz, 1 H), 7.45 (m, 1 H) ppm. FAB+: *m/z* 209.1 [MH⁺]. C₁₂H₈N₄ (208.22) + 0.025 CHCl₃: calcd. C 68.38, H 3.83, N 26.53; found C 68.42, H 3.85, N 26.53.

6-Amino-2,2'-bipyridinyl-5-carbaldehyde (9): A solution of 7-(pyridin-2-yl)pyrido[2,3-*d*]pyrimidine (229 mg, 1.1 mmol) in 2 N aqueous hydrochloric acid (80 mL) was refluxed for 2.5 h and then cooled in ice. The solution was neutralized with concentrated aqueous

ammonia (pH ca. 8–9), extracted with ethyl acetate (3 × 50 mL), and the combined organic layers were dried (Na₂SO₄), concentrated, and the brown residue purified by column chromatography (basic alumina, CH₂Cl₂/EtOAc) to give 180 mg (82%) of the desired amino aldehyde as a yellow powder (m.p. 143 °C). ¹H NMR (CDCl₃): δ = 9.90 (s, 1 H), 8.70 (br. d, ³*J* = 4.3 Hz, 1 H), 8.36 (d, ³*J* = 8.0 Hz, 1 H), 7.94 (d, ³*J* = 7.9 Hz, 1 H), 7.85 (d, ³*J* = 7.7 Hz, 1 H), 7.81 (br. t, ³*J* = 8.0 Hz, 1 H), 7.33 (ddd, ³*J*_{5',4'} = 7.5, ³*J*_{5',6'} = 4.8, ⁴*J*_{5',3'} = 1.4 Hz, 1 H) ppm. ¹³C NMR (CDCl₃): δ = 192.3, 160.2, 158.0, 155.1, 149.3, 145.0, 136.8, 124.5, 122.1, 113.8, 110.6 ppm. FAB+: *m/z* 200.1 [MH⁺]. C₁₁H₉N₃O (199.21) + 0.064 EtOAc: calcd. C 66.00, H 4.68, N 20.51, O 8.81; found C 66.00, H 4.62, N 20.50.

2,7-Dipyridin-2-yl[1,8]naphthyridine (bpnp): Two drops of a 10% methanolic potassium hydroxide solution were added to a hot solution of 6-amino-2,2'-bipyridinyl-5-carbaldehyde (3; 75 mg, 3.76 × 10^{−4} mol) and 2-acetylpyridine (51 mg, 4.21 × 10^{−4} mol, 1.1 equiv.) in absolute ethanol (15 mL). The solution was further refluxed for 6 h under dinitrogen. The solvent was evaporated and the solid taken up in dichloromethane (35 mL) and washed with water (10 mL). The aqueous layer was extracted with dichloromethane (5 mL) and the combined organic layers washed with brine (15 mL), dried (Na₂SO₄), filtered, concentrated, purified by column chromatography (basic Al₂O₃, CH₂Cl₂), and washed with acetone and diethyl ether to yield an off-white solid (88 mg, 82%). ¹H NMR (CDCl₃): δ = 8.89 (d, ³*J* = 8.0 Hz, 2 H), 8.75 (d, ³*J* = 8.5 Hz, 2 H), 8.8 (m, 2 H), 8.36 (d, ³*J* = 8.5 Hz, 2 H), 7.92 (td, ³*J* = 7.7, ⁴*J* = 1.7 Hz, 2 H), 7.41 (ddd, ³*J* = 7.5, ³*J* = 4.8, ⁴*J* = 1.0 Hz, 2 H) ppm.

4-*tert*-Butylbenzamide Hydrochloride (2):^[38] Gaseous hydrogen chloride was bubbled into a solution of 4-*tert*-butylbenzonitrile (1; 15.94 g, 0.10 mol) in a mixture of dry benzene (25 mL) and absolute ethanol (20 mL) until saturation was attained. The solution was stirred for an hour and left to stand at room temperature for three days. The solution was then concentrated to half its volume in vacuo until white crystals appeared. The flask was cooled in ice and diethyl ether was added. The white solid was then filtered and washed with diethyl ether (3 × 15 mL) and dried in vacuo. It was then suspended in absolute ethanol (40 mL) and 60 mL of ammonia-saturated ethanol was added. A white precipitate formed immediately and the reaction mixture was stirred for a day and left to stand for four days. The white suspension was filtered and the filtrate concentrated in vacuo. The solid residue was then collected and washed with diethyl ether and dried in vacuo to yield 16.71 g [78%; m.p. 155 °C (dec.)] of the desired amidine hydrochloride as a white solid. ¹H NMR ([D₆]DMSO): δ = 9.5 (br. s, 2 H), 9.3 (br. s, 2 H), 7.85 (d, ³*J* = 8.6 Hz, 2 H), 7.62 (d, ³*J* = 8.6 Hz, 2 H), 1.30 (s, 9 H) ppm. ¹³C NMR ([D₆]DMSO): δ = 165.4, 156.9, 127.9, 125.7, 124.9, 34.8, 30.6 ppm. IR (KBr): $\tilde{\nu}$ = 3061 (F), 1674 (m), 1486 (m), 852 (f), 734 (f), 674 (f), 557 (f), 210 (m) cm^{−1}. FAB+: *m/z* 177.2 [C₁₁H₁₇N₂]⁺. C₁₁H₁₇ClN₂ (212.72): calcd. C 62.11, H 8.06, N 13.17; found C 62.20, H 7.92, N 13.14.

2-(4-*tert*-Butylphenyl)-4,6-dihydroxypyrimidine (3):^[39] A freshly prepared solution of sodium methoxide (6.6 g sodium in 75 mL absolute methanol) was added dropwise, at room temperature, to a suspension of 4-*tert*-butylbenzamide hydrochloride (16.71 g, 79 mmol) and diethyl malonate (12.8 mL, 84 mmol, 1.07 equiv.) in absolute ethanol (150 mL). The mixture was refluxed under dinitrogen for 7 h. The volatile solvents were removed and the pinkish residue taken up in water (120 mL) and acidified to pH 3–4 with concentrated hydrochloric acid (ca. 20 mL). The pale-yellow precipitate was filtered and washed with water (2 × 20 mL), dried in

air and in vacuo to yield 18.4 g of 2-(4-*tert*-butylphenyl)-4,6-dihydroxypyrimidine [92%, m.p. > 260 °C (dec.)]. ¹H NMR ([D₆]-DMSO): δ = 8.8 (br. s, 1 H), 8.05 (d, ³J = 8.5 Hz, 2 H), 7.54 (d, ³J = 8.6 Hz, 2 H), 5.32 (s, 1 H), 1.31 (s, 9 H) ppm. ¹³C NMR ([D₆]-DMSO): δ = 167.3, 157.2, 154.6, 129.3, 127.5, 125.3, 88.1, 34.6, 30.8 ppm. IR (KBr): ν̄ = 2962 (m), 1637 (F), 1325 (m), 1268 (m), 1197 (f), 844 (f), 520 (f) cm⁻¹. FAB+: *m/z* 245.2 [MH⁺]. C₁₄H₁₆N₂O₂ (244.29): calcd. C 68.83, H 6.60, N 11.47, O 13.10; found C 68.79, H 6.60, N 11.33.

2-(4-*tert*-Butylphenyl)-4,6-dichloropyrimidine (4Ph):^[39] Phosphoryl chloride (21 mL, 0.23 mol, 5.3 equiv.) was added dropwise followed by 2-(4-*tert*-butylphenyl)-4,6-dihydroxypyrimidine (10.34 g, 42.3 mmol) portionwise to *N,N*-dimethylaniline (9.2 mL, 73 mmol, 1.7 equiv.) at room temperature under argon. The brown mixture was allowed to warm up whereupon it turned reddish. The mixture was refluxed for 1.25 h, then allowed to cool and cautiously poured onto ice (ca. 80 g). The pinkish solid was filtered, washed with water until the filtrate was colorless, dried in air and in vacuo, and purified by flash chromatography (SiO₂; hexane/CH₂Cl₂, 80:6 to 40:7) to yield 21.6 g of a crystalline white solid (92%, m.p. 93 °C). ¹H NMR (CDCl₃): δ = 8.35 (d, ³J = 8.6 Hz, 2 H), 7.51 (d, ³J = 8.7 Hz, 2 H), 7.22 (s, 1 H), 1.37 (s, 9 H, CH₃) ppm. ¹³C NMR (CDCl₃): δ = 165.9, 162.0, 156.0, 132.3, 128.8, 125.8, 118.4, 35.1, 31.3 ppm. *R*_f (SiO₂; hexane/CH₂Cl₂, 2.0:0.3) = 0.47. IR (KBr): ν̄ = 2964 (f), 1551 (F), 1519 (F), 1387 (m), 1248 (f), 1097 (f), 830 (m), 642 (f), 218 (F) cm⁻¹. FAB+: *m/z* 281.1 [MH⁺]. C₁₄H₁₄Cl₂N₂ (280.05): calcd. C 59.96, H 5.04, N 10.05, Cl 25.31; found C 59.91, H 5.02, N 9.85.

1-[6-Acetyl-2-(4-*tert*-butylphenyl)pyrimidin-4-yl]ethyl Ketone (5Ph):^[20] Dichlorobis(triphenylphosphane)palladium(II) (450 mg) was added to a solution of 2-(4-*tert*-butylphenyl)-4,6-dichloropyrimidine (4Ph; 6.0 g, 21.3 mmol) and (1-ethoxyvinyl)tri(*n*-butyl)-stannane^[20] (17.68 g, 49 mmol, 2.3 equiv.) in dry DMF (90 mL). The solution was heated at 80 °C under argon for 12 h. At room temperature, the black solution was poured into an aqueous solution of potassium fluoride (20 g KF in 200 mL of water). The brown precipitate was filtered and washed with diethyl ether (300 mL and 4 × 80 mL). The organic layer was washed with brine (6 × 40 mL), dried (Na₂SO₄), filtered, and concentrated. The resulting beige solid was purified by flash chromatography (SiO₂; hexane/diethyl ether, 95:5) to yield 7.22 g of the bis(vinyl) ether as a pale-yellow solid (97%). The latter (5.11 g, 14.5 mmol) was dissolved in acetone (80 mL), 2 N aqueous HCl (15 mL) was added, and the solution stirred at room temperature for 6 h. The volatile solvent was removed and the white residual solid taken up in dichloromethane (200 mL) and washed with an aqueous saturated solution of sodium hydrogen carbonate (60 mL). The aqueous layer was extracted with dichloromethane (3 × 20 mL) and the combined organic layers dried (Na₂SO₄), filtered, concentrated, and purified by flash chromatography (SiO₂; hexane/CH₂Cl₂, 1.0:2.0) to yield the desired bis-acetylated arylchloropyrimidine (4.1 g, 95%, m.p. 136 °C). ¹H NMR (CDCl₃): δ = 8.50 (d, ³J = 8.6 Hz, 2 H), 8.25 (s, 1 H), 7.58 (d, ³J = 8.6 Hz, 2 H), 2.83 (s, 6 H), 1.40 (s, 9 H) ppm. ¹³C NMR (CDCl₃): δ = 199.2, 165.4, 161.4, 155.4, 133.6, 128.4, 125.9, 110.5, 35.1, 31.3, 25.8 ppm. *R*_f (SiO₂; hexane/CH₂Cl₂, 1.0:2.0) = 0.30. IR (KBr): ν̄ = 2963 (m), 1712 (F), 1551 (F), 1419 (F), 1355 (F), 1239 (F), 1182 (F), 854 (m), 790 (m), 565 (m), 210 (F) cm⁻¹. FAB+: *m/z* 297.4 [MH⁺]. C₁₈H₂₀N₂O₂ (296.36): calcd. C 72.94, H 6.81, N 9.46, O 10.8; found C 72.84, H 6.79, N 9.61.

4,6-Bis(2-amino-3-formylpyridyl)-2-(4-*tert*-butylphenyl)pyrimidine (7Ph):^[40] Five drops of a 10% methanolic potassium hydroxide solution were added to a solution of 1-[6-acetyl-2-(4-*tert*-bu-

tylphenyl)pyrimidin-4-yl] ethyl ketone (5Ph; 1.00 g, 3.41 mmol) and 4-aminopyrimidine-5-carboxaldehyde (890 mg, 7.23 mmol, 2.1 equiv.) in absolute ethanol (100 mL) at reflux under argon. The solution rapidly turned brown and a beige precipitate appeared. The mixture was refluxed for 8 h, cooled to room temperature, and the precipitate was centrifuged and dried in vacuo. It was then suspended in 2 N aqueous HCl (340 mL) and vigorously stirred at reflux for 5 h. At room temperature, the mixture was neutralized with concentrated ammonia. The orange suspension was filtered, washed with water (2 × 15 mL), dried in vacuo, and purified by flash chromatography (SiO₂; CH₂Cl₂/EtOAc, 400:15 to 400:40) to yield the desired bis(aminoaldehyde) [1.1 g, 70%, m.p. > 260 °C (dec.)] as a yellow solid. A sample was recrystallized from dichloromethane/hexane for analysis. ¹H NMR (CDCl₃): δ = 9.99 (s, 2 H), 9.11 (s, 1 H), 8.60 (d, ³J = 8.5 Hz, 2 H), 8.16 (d, ³J = 7.4 Hz, 2 H), 8.01 (d, ³J = 7.6 Hz, 2 H), 7.59 (br. s), 7.59 (d, ³J = 8.5 Hz, 2 H), 6.86 (br. s, 4 H), 1.43 (s, 9 H) ppm. ¹³C NMR ([D₆]DMSO): δ = 193.4, 163.3, 163.0, 157.8, 157.0, 153.9, 146.2, 134.1, 127.9, 125.5, 114.6, 111.8, 110.0, 34.6, 30.9 ppm. *R*_f (SiO₂; CH₂Cl₂/EtOAc, 2.0:0.3) = 0.46. IR (KBr): ν̄ = 3349 (m), 2961 (m), 1671 (m), 1619 (m), 1581 (m), 1534 (F), 1379 (m), 1211 (m), 795 (m), 210 (F) cm⁻¹. FAB+: *m/z* 453.0 [MH⁺]. C₂₆H₂₄N₆O₂ (452.51) + 0.37hexane: calcd. C 69.97, H 6.07, N 17.35, O 6.61; found C 69.97, H 6.07, N 16.53.

2-(4-*tert*-Butylphenyl)-4,6-bis(7-pyridin-2-yl)[1,8]naphthyridin-2-yl-pyrimidine (LPh): Two drops of a 10% methanolic potassium hydroxide solution were added to a hot solution of bis(aminoaldehyde) 7Ph (150 mg, 3.31 × 10⁻⁴ mol) and 2-acetylpyridine (103 mg, 8.5 × 10⁻⁴ mol, 2.6 equiv.) in pyridine (26 mL) and the solution stirred at 75 °C for 22 h. The solvent was removed in vacuo and the solid taken up in chloroform (60 mL), which was successively washed with water (20 mL), brine (15 mL), dried (Na₂SO₄), filtered, and concentrated. The residue was washed with acetone to yield an off-white solid (184 mg, 90%; m.p. > 260 °C), which was recrystallized from chloroform and acetone and then purified by flash chromatography (SiO₂; CH₂Cl₂/CH₃OH, 1.0:0.1). ¹H NMR (CDCl₃): δ = 10.06 (s, 1 H), 9.0 (br. d, ³J = 8.4 Hz, 4 H), 8.81 (d, ³J = 8.4 Hz, 2 H), 8.8 (m, 2 H), 8.73 (d, ³J = 8.5 Hz, 2 H), 8.47 (d, ³J = 8.5 Hz, 2 H), 8.42 (d, ³J = 8.6 Hz, 2 H), 7.97 (td, ³J = 7.7, ⁴J = 1.8 Hz, 2 H), 7.64 (d, ³J = 8.5 Hz, 2 H), 7.43 (ddd, ³J = 7.5, ³J = 4.8, ³J = 1.1 Hz, 2 H), 1.44 (s, 9 H) ppm. IR (KBr): ν̄ = 1604 (F), 1525 (F), 1469 (f), 1427 (m), 1371 (f), 862 (f), 792 (m), 409 (f) cm⁻¹. FAB+: *m/z* 623.1 [MH⁺], 645.3 [MNa⁺]. C₄₀H₃₀N₈ (622.72) + 0.32 CHCl₃: calcd. C 74.55, H 4.70, N 17.30; found C 74.49, H 4.83, N 17.09. UV/Vis (CH₂Cl₂): λ_{max} (log ε) = 253 nm (4.95), 273 (sh, 4.8), 293 (sh, 4.6), 331 (sh, 4.4), 344 (4.56), 363 (4.48).

1-[6-Acetyl-2-(anthracen-9-yl)pyrimidin-4-yl]ethyl Ketone (5Ant): 2-Anthracen-9-yl-4,6-dichloropyrimidine 4Ant (986 mg, 3.03 mmol)^[26b] and 1-(tri-*n*-butylstannyl)-1-vinyl ethyl ether (2.40 g, 6.66 mmol, 2.2 equiv.) were suspended in 15 mL of DMF. After purging three times with argon, dichlorobis(triphenylphosphane)palladium(II) (64 mg, 9.1 × 10⁻⁵ mol, 0.03 equiv.) was added and the mixture heated to 80 °C under argon for 12 h whilst being protected from light. The solvent was removed in vacuo and the brown residue taken up in dichloromethane (50 mL) and washed with water (3 × 40 mL). The organic layer was dried (Na₂SO₄), filtered, concentrated, and purified by flash chromatography (SiO₂; hexane/CH₂Cl₂, 1.0:1.0) to yield 1.078 g of the desired bis(vinyl ether) as a yellow solid (90%). ¹H NMR (CDCl₃): δ = 8.55 (s, 1 H), 8.05 (s, 1 H), 8.05 (d, ³J = 8.3 Hz, 2 H), 7.70 (d, ³J = 8.6 Hz, 2 H), 7.3–7.6 (m, 4 H), 5.66 (d, ²J = 2.0 Hz, 2 H), 4.49 (d, ²J = 2.0 Hz, 2 H), 4.05 (q, ³J = 7.0 Hz, 4 H), 1.52 (t, ³J = 7.0 Hz, 6 H) ppm. ¹³C

NMR (CDCl₃): δ = 165.5, 162.1, 157.1, 134.2, 131.5, 129.9, 128.4, 128.0, 126.1, 125.9, 125.1, 108.2, 88.5, 63.8, 14.5 ppm. R_f (SiO₂; hexane/CH₂Cl₂, 1.0:1.0) = 0.40.

2 N Hydrochloric acid (6 mL) was added to a mixture of this bis(vinyl ether) in acetone/THF (25/10 mL) and the mixture stirred at room temperature for 12 h. The volatiles were evaporated and the residue taken up in dichloromethane (50 mL) and washed with an aqueous saturated sodium hydrogen carbonate solution (2 × 10 mL). The combined aqueous layers were extracted with dichloromethane (2 × 10 mL), and the combined organic layers dried (Na₂SO₄), filtered, concentrated, and purified by flash chromatography (SiO₂; hexane/CH₂Cl₂, 1.0:2.0) to yield 828 mg of a yellow solid [90%; m.p. 228 °C (dec.)], which was recrystallized from chloroform/diethyl ether. ¹H NMR (CDCl₃): δ = 8.66 (s, 1 H), 8.57 (s, 1 H), 8.12 (d, ³J = 8.4 Hz, 2 H), 7.4–7.6 (m, 6 H), 2.72 (s, 6 H) ppm. ¹³C NMR (CDCl₃): δ = 199.0, 168.0, 161.6, 132.3, 131.3, 129.9, 129.1, 128.8, 126.6, 125.4, 125.1, 111.2, 25.9 ppm. R_f (SiO₂; hexane/CH₂Cl₂, 1.0:2.0) = 0.36. EI-MS: m/z 340.3 [M⁺], 297.3 [M – COCH₃]⁺, 255.3 [M – 2 COCH₃]⁺. C₂₂H₁₆N₂O₂ (340.37) + 0.075 CH₂Cl₂: calcd. C 76.46, H 4.69, N 8.08, O 9.23; found C 76.50, H 4.62, N 8.06.

2-(Anthracen-9-yl)-4,6-bis(7-pyridin-2-yl)[1,8]naphthyridin-2-ylpyrimidine (LAnt): One drop of a 10% methanolic potassium hydroxide solution was added to a hot solution (65 °C) of the diketone **5Ant** (45 mg, 1.32 × 10^{−4} mol) and 6-amino-2,2'-bipyridinyl-5-carbaldehyde (54 mg, 2.71 × 10^{−4} mol, 2.05 equiv.) in pyridine (10 mL). The solution was stirred at this temperature for 11 h. The solvent was then removed in vacuo and the solid taken up in dichloromethane (40 mL), washed with water (10 then 15 mL), dried (Na₂SO₄), filtered, and concentrated. The crude was purified by column chromatography (basic alumina) and recrystallized by diffusion of acetone into a concentrated chloroform solution to yield a pale-yellow solid (63 mg, 72%, m.p. > 260 °C). ¹H NMR (CDCl₃): δ = 10.3 (s, 1 H), 9.03 (d, ³J = 7.9 Hz, 2 H), 8.7–8.85 (m, ³J = 8.4 Hz, 6 H), 8.67 (s, 1 H), 8.39 (d, ³J = 9.1 Hz, 2 H), 8.34 (d, ³J = 8.7 Hz, 2 H), 8.14 (br. d, ³J = 7.6 Hz, 2 H), 7.99 (td, ³J = 7.8, ⁴J = 1.8 Hz, 2 H), 7.88 (br. d, ³J = 8.6 Hz, 2 H), 7.4–7.6 (m, 6 H) ppm. ¹³C NMR (CDCl₃): δ = 164.7, 164.6, 160.3, 158.0, 157.3, 155.6, 149.2, 138.1, 137.7, 137.2, 131.6, 130.1, 128.6, 128.0, 127.8, 126.3, 125.3, 124.8, 123.9, 123.0, 121.1, 120.9, 120.7, 114.7 ppm. IR (KBr): $\tilde{\nu}$ = 1601 (F), 1523 (F), 1467 (f), 1426 (m), 1379 (f), 865 (f), 783 (m), 739 (f), 413 (f) cm^{−1}. FAB⁺: m/z 667.3 [MH⁺]. C₄₄H₂₆N₈ (666.73) + 0.90 CHCl₃: calcd. C 72.55, H 3.63, N 15.18; found C 72.61, H 3.57, N 15.18. UV/Vis (CH₂Cl₂): $\lambda_{\max}$ (log ϵ) = 250 nm (sh, 5.0), 256 (5.14), 275 (sh, 4.5), 320 (sh, 4.1), 333 (sh, 4.3), 347 (4.46), 363 (4.47), 385 (3.88). Fluorescence (CH₂Cl₂): $\lambda_{\max}$ (emission) = 331, 356, 376 (sh) nm.

[(CH₃COO)₃Rh₂]₂LPh](PF₆)₂ [(Rh₂)₂LPh]:^[22a] 1.0 N Aqueous hydrochloric acid (66 μ L, 6.6 × 10^{−5} mol, 2.0 equiv.) was added to a suspension of ligand LPh (20.5 mg, 3.29 × 10^{−5} mol) and dirhodium tetraacetate (29.9 mg, 6.6 × 10^{−5} mol, 2.0 equiv.) in methanol (7 mL) under argon and the mixture was heated to 50 °C for 12 h. The deep green solution was filtered and ammonium hexafluorophosphate (51 mg, 3.1 × 10^{−4} mol, 9.5 equiv.) in water (1 mL) was added. The solvent was then evaporated and diethyl ether allowed to diffuse into a concentrated solution of the residue in acetonitrile. The precipitate was filtered and washed with water and diethyl ether to yield a deep green solid (47 mg, 85%, m.p. > 260 °C). ¹H NMR (CD₃CN): δ = 9.71 (s, 1 H), 9.67 (br. d, ³J = 4.4 Hz, 2 H), 9.24 (d, ³J = 8.8 Hz, 2 H), 8.8–9.0 (m, 10 H), 8.58 (td, ³J = 8.0, ⁴J = 1.5 Hz, 2 H), 8.29 (dd, ³J = 7.5, ³J = 4.7 Hz, 2 H), 7.75 (d, ³J = 8.8 Hz, 2 H), 1.49 (s, 15 H), 1.27 (s, 12 H) ppm. IR (KBr): $\tilde{\nu}$ = 3450 (F),

1604 (f), 1564 (F), 1437 (f), 1158 (f), 1021 (f), 846 (F), 705 (f), 560 (f), 405 (m) cm^{−1}. ES-MS (CH₃CN, 100 V): m/z 694.0 [(Rh₂)₂-LPh]²⁺, 1532.8 [(Rh₂)₂LPh, PF₆]⁺. UV/Vis (CH₃CN): $\lambda_{\max}$ (log ϵ) = 250 nm (4.9), 292 (4.6), 347 (sh, 4.5), 371 (4.6), 412 (sh, 4.2), 468 (4.0), 543 (3.7), 622 (3.7). $E_{1/2}$ (V vs. SCE, CH₂Cl₂, 0 °C): −1.72 (rev.), −1.41 (rev.), −1.20 (rev.), −0.60 (rev.), −0.22 (rev.), 1.46 (rev.).

[(CH₃COO)₃Rh₂]₂LAnt](PF₆)₂ [(Rh₂)₂LAnt]:^[22a] The same protocol as above starting from ligand LAnt yielded a brown-green product with a similar yield after precipitation of the hexafluorophosphate salt from a methanolic solution. (m.p. > 260 °C) ¹H NMR (CD₃CN): δ = 10.13 (s, 1 H), 9.50 (br. d, ³J = 5 Hz, 2 H), 9.47 (d, ³J = 8.8 Hz, 2 H), 8.8–9.1 (m, 9 H), 8.52 (td, ³J = 7.7, ⁴J = 1.4 Hz, 2 H), 8.2–8.3 (m, 4 H), 7.92 (d, ³J = 8.4 Hz, 2 H), 7.47 (br. t, ³J = 8.4 Hz, 2 H), 7.31 (br. t, ³J = 7.3 Hz, 2 H), 1.33 (s, 6 H), 1.21 (s, 12 H) ppm. IR (KBr): $\tilde{\nu}$ = 3450 (F), 1605 (f), 1565 (F), 1437 (m), 1414 (m), 1154 (f), 1017 (f), 845 (F), 704 (f), 559 (f), 406 (m) cm^{−1}. ES-MS (CH₃CN, 20 V): m/z 716.0 [(Rh₂)₂LAnt]²⁺, 1576.9 [(Rh₂)₂-LAnt, PF₆]⁺. C₅₆H₄₄F₁₂N₈O₁₂P₂Rh₄·2.6 CH₃OH: calcd. C 38.98, H 3.04, N 6.21; found C 39.24, H 3.05, N 6.65. UV/Vis (CH₃CN): $\lambda_{\max}$ (log ϵ) = 248 nm (3.1), 254 (5.2), 295 (4.5), 347 (sh, 4.5), 364 (4.6), 382 (4.8), 478 (4.1), 545 (3.8), 634 (3.8). $E_{1/2}$ (V vs. SCE, CH₃CN, 25 °C): −0.30 (rev.), 0.73 (rev.), 0.86 (rev.), 1.51 (irrev.).

[(CH₃COO)₃Ru₂]₂LPh](PF₆)₂ [(Ru₂)₂LPh]:^[22b] A suspension of ligand LPh (14 mg, 2.25 × 10^{−5} mol) and [Ru₂(CH₃COO)₄Cl] (21.8 mg, 4.60 × 10^{−5} mol, 2.05 equiv.) in methanol (5 mL) was heated at 50 °C under argon for 48 h. After cooling to room temperature, the hexafluorophosphate salt was precipitated by addition of ammonium hexafluorophosphate (38 mg in 1 mL of degassed water, 2.33 × 10^{−4} mol, 10 equiv.). The solid was washed with methanol and diethyl ether and dried in vacuo to yield 28 mg of a dark blue paramagnetic powder (75%; m.p. > 260 °C). ¹H NMR (CD₃OD, before addition of NH₄PF₆): δ = 72.0, 66.7, 29.9, 25.7, 16.9, 8.8, 4.1, 2.0, 1.25, −3.8, −7.3, −13.3, −15.4, −22.0, −39.8 ppm. IR (KBr): $\tilde{\nu}$ = 3450 (F), 1593 (f), 1536 (m), 1437 (F), 1329 (f), 1197 (f), 1018 (f), 843 (F), 777 (f), 691 (f), 558 (f), 407 (m) cm^{−1}. ES-MS (CH₃CN): m/z 691.0 [(Ru₂)₂LPh]²⁺, 1527 [(Ru₂)₂LPh, PF₆]⁺, 460.4 [(Ru₂)₂LPh]³⁺. C₅₂H₄₈F₁₂N₈O₁₂P₂Ru₄·2.65 H₂O: calcd. C 36.33, H 3.13, N 6.52; found C 36.33, H 3.26, N 6.59. UV/Vis (CH₃CN): $\lambda_{\max}$ (log ϵ) = 248 nm (4.8), 270 (sh, 4.6), 370 (4.6), 400 (sh, 4.4), 600 (4.0), 695 (4.2). $E_{1/2}$ (V vs. SCE, degassed CH₃CN, 25 °C): −0.31 (rev.), 0.76 (rev.), 0.85 (rev.).

[(CH₃COO)₃Ru₂]₂LAnt](PF₆)₂ [(Ru₂)₂LAnt]:^[22b] A suspension of ligand LAnt (19.6 mg, 2.94 × 10^{−5} mol) and [Ru₂(OAc)₄Cl] (30.2 mg, 6.37 × 10^{−5} mol, 2.17 equiv.) in degassed methanol (6.5 mL) was heated at 50 °C under argon for 44 h. After cooling to room temperature, the hexafluorophosphate salt was precipitated by addition of ammonium hexafluorophosphate (53 mg in 1.3 mL of degassed water, 3.25 × 10^{−4} mol, 11 equiv.). The solid was washed with methanol and diethyl ether, and dried in vacuo to yield 40 mg of a deep blue paramagnetic compound (79%; m.p. > 260 °C). ¹H NMR (CD₃OD, before addition of NH₄PF₆): δ = 75.1, 69.8, 29.9, 36.3, 25.0, 17.7, 10.7, 9.8, 5.3, 2.0, −5.0, −8.3, −14.5, −16.5, −16.9, −20.0, −35.6 ppm. IR (KBr): $\tilde{\nu}$ = 3448 (F), 1630 (f), 1597 (f), 1535 (m), 1437 (F), 1329 (f), 1266 (f), 1213 (f), 844 (F), 776 (f), 691 (m), 559 (f), 406 (f) cm^{−1}. ES-MS (CH₃CN, 20 V): m/z 713.1 [(Ru₂)₂LAnt]²⁺, 1570 [(Ru₂)₂LAnt, PF₆]⁺, 475.3 [(Ru₂)₂-LAnt]³⁺. C₅₆H₄₄F₁₂N₈O₁₂P₂Ru₄·2.2 H₂O: calcd. C 38.33, H 2.78, N 6.39; found C 38.33, H 2.92, N 6.37. UV/Vis (CH₃CN): $\lambda_{\max}$ (log ϵ) = 254 nm (4.7), 369 (4.5), 387 (4.6), 602 (4.0), 701 (4.2). $E_{1/2}$ (V vs. SCE, degassed CH₃CN, 25 °C): −0.30 (rev.), 0.73 (rev.), 0.86 (rev.), 1.51 (irrev.).

Supporting Information (see also the footnote on the first page of this article): Figures S1 and S2 show differential pulse voltammog-

rams of complexes $[(\text{Rh}_2)\text{LPh}(\text{Rh}_2)]$ and $[(\text{Ru}_2)\text{LPh}(\text{Ru}_2)]$, respectively, in acetonitrile.

Acknowledgments

A. P. acknowledges the support the French ministère de l'Éducation Nationale, de la Recherche et de la Technologie for a PhD fellowship. The Italian team thanks the University of Bologna ("Funds for selected topics") and the University of Messina for financial support.

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Received: May 19, 2006

Published Online: August 15, 2006