Inorg. Chem. **1995,** *34,* 541−545

Absorption Spectra, Luminescence Properties, and Electrochemical Behavior of Cyclometalated Iridium(III) and Rhodium(III) Complexes with a Bis(pyridyl)triazole Ligand

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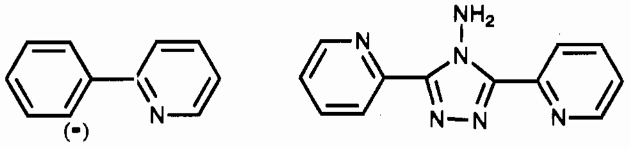
Received July 22, 1994⊛

Two new cyclometalated Rh(III) and Ir(III) complexes have been synthesized, and their absorption spectra, luminescence properties (in rigid matrix at 77 K and in fluid solution at room temperature), and electrochemical behavior have been investigated and compared to those of other similar Rh(III) and Ir(III) cyclometalated species. The new compounds are $[Rh(ppy)_2(dpt\text{-}NH_2)](PF_6)$ (**1**) and $[Ir(ppy)_2(dpt\text{-}NH_2)](PF_6)$ (**2**) (ppy = phenylpyridine anion; dpt-NH_2 = 4-amino-3,5-bis(2-pyridyl)-4*H*-1,2,4-triazole). The absorption spectra of the compounds are dominated by intense ligand-centered bands in the UV region (ϵ_{max} in the range 10^4-10^5 M^{-1} cm^{-1}) and by moderately intense metal-to-ligand charge transfer bands in the visible region (ϵ_{max} in the range 10^3-10^4 M^{-1} cm^{-1}). A reversible oxidation occurs for **2** at +1.23 V *vs* SCE, assigned to removal of an electron from a metal-centered $d\pi$ orbital, while an irreversible oxidation is observed for **1** at more positive potentials ($E_{peak} = +1.51$ V *vs* SCE), assigned to removal of an electron from a metal−ligand (C^-) σ-bonding orbital. Both complexes are luminescent in rigid matrices at 77 K (**1**, $\lambda_{max} = 458$ nm, $\tau = 160$ μs; **2**, $\lambda_{max} = 475$ nm, $\tau = 5.8$ μs), while only the Ir compound emits in fluid solution at room temperature ($\lambda_{max} = 560$ nm, $\tau = 870$ ns, $\Phi = 0.246$). The emission originates from a metal-perturbed, triplet ppy-centered excited state for the Rh species, while a triplet MLCT level is responsible for the emission of the Ir compound. The results obtained are a step toward the preparation of photoactive and redox-active multinuclear compounds based on bis(pyridyl)triazole derivative bridges and incorporating Ir(III) and Rh(III) cyclometalated building blocks.

Introduction

In the last 10 years cyclometalated complexes of Ir(III) and Rh(III) have been at the center of a large interest because of their outstanding photophysical and electrochemical properties,[1−7] which make this family of compounds quite promising for photochemical energy conversion studies. In very recent times, Ir(III) and Rh(III) cyclometalated species were also investigated as parts of more complicated supramolecular species featuring photoinduced energy and electron transfer processes.[8,9]

Multichelating ligands made of 3,5-bis(2-pyridyl)-1,2,4-triazole moieties connected by cyclohexyl derivative spacers (synthesized by a simple and efficient route from 4-amino-3,5-bis(2-pyridyl)-4*H*-1,2,4-triazole) were recently investigated by our research group,[10] and the results obtained indicate that such species can be considered suitable bridging ligands to arrange metal complexes in a supramolecular fashion.



ppy dpt-NH_2

Figure 1. Structural formulas of the ligands.

Here we report the synthesis and the absorption spectra, luminescence properties, and electrochemical behavior of two new Ir(III) and Rh(III) cyclometalated species with the 3,5-bis(2-pyridyl)-1,2,4-triazole moiety as the polypyridine ligand. The complexes investigated are $[Rh(ppy)_2(dpt\text{-}NH_2)]^+$ and $[Ir(ppy)_2(dpt\text{-}NH_2)]^+$ (ppy = 2-phenylpyridine anion; dpt-NH_2 = 4-amino-3,5-bis(2-pyridyl)-4*H*-1,2,4-triazole; for structural formulas of the ligands, see Figure 1). The information obtained from this paper represents a step toward the preparation of photoactive and redox-active multinuclear compounds based on bis(pyridyl)-triazole derivative bridges and incorporating Ir(III) and Rh(III) cyclometalated building blocks.

Experimental Section

Materials and Methods. The precursor complexes $[Ir(ppy)_2Cl]_2$[11] and $[Rh(ppy)_2Cl]_2$[11] were prepared by following literature procedures. The other chemicals used were of the best commercial grade and were

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⊛ Abstract published in *Advance ACS Abstracts,* November 15, 1994.

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employed without further purifications. Absorption spectra were recorded on a Kontron Uvikon 860 spectrophotometer. Luminescence spectra and lifetimes were measured with a Perkin-Elmer LS-5B spectrofluorimeter equipped with a red-sensitive Hamamatsu R928 photomultiplier and with an Edinburgh FL-900 single-photon-counting spectrometer, respectively. Luminescence quantum yields were measured at room temperature (20 °C) with the optically dilute method,[12] calibrating the spectrofluorimeter with a standard lamp and using $[Ru(bpy)_3]^{2+}$ in aerated acqueous solution as a quantum yield standard ($\Phi = 0.028$[13]).When necessary, samples were deoxygenated by bubbling nitrogen for at least 20 min. Electrochemical measurements were carried out in argon-purged acetonitrile at room temperature with PAR 273 multipurpose equipment interfaced to a PC. The working electrode was a Pt microelectrode or a glassy carbon (8 mm^2, Amel) electrode. The counter electrode was a Pt wire, and the reference electrode was a SCE separated with a fine glass frit. The concentration of the complexes was 5×10^{-4} M. Tetraethylammonium hexafluorophosphate was used as supporting electrolyte, and its concentration was 0.05 M. Cyclic voltammograms were obtained at scan rates of 50, 500, and 1000 mV/s. For reversible processes, half-wave potentials (*vs* SCE) were calculated as an average of the cathodic and anodic peaks. The criteria for reversibility were the separation between cathodic and anodic peaks, the close to unity ratio of the intensities of the cathodic and anodic currents, and the constancy of the peak potential on changing scan rate. The number of exchanged electrons was measured with differential pulse voltammetry (DPV) experiments performed with a scan rate of 20 mV/s, a pulse height of 75 mV, and a duration of 40 ms. The procedure for the calibration of the number of electrons corresponding to the various redox waves has been described in detail.[14,15]

Experimental errors in the reported data are as follows: absorption maxima, 2 nm; emission maxima, 4 nm; molar absorption coefficients, 10%; emission lifetimes, 10%; emission quantum yields, 20%; redox potentials, 20 mV.

Preparation of the Complexes. $[Rh(ppy)_2(dpt\text{-}NH_2)](PF_6)$ (1). The dinuclear precursor complex $[Rh(ppy)_2Cl]_2$[11] (0.020 g, 0.02 mmol) was dissolved in dichloromethane (4 mL), and this solution was added to a refluxing dichloromethane solution (5 mL) of dpt-NH_2 (0.0097 g, 0.04 mmol). After the mixture was refluxed for 1 h, it was cooled to room temperature and rotary-evaporated in vacuo to reduce the solvent to 2 mL. A saturated solution of KPF_6 in methanol (1.5 mL) was added. The mixture was rotary-evaporated in vacuo until the precipitation began to appear. The product was filtered off, recrystallized in dichloromethane/methanol 1:1 (v/v), and vacuum-dried (yield 0.028 g, 87%). Color: yellow. Typical IR bands (KBr pellets, cm^{-1}): 1607 (m), 1482 (m), 1455 (w), 1428 (w), 842 (s), 755 (m), 558 (m). Anal. Found (calc) for $[Rh(ppy)_2(dpt\text{-}NH_2)](PF_6)$: C, 51.3 (51.4); H, 3.3 (3.3); N, 13.9 (14.1). Λ (5×10^{-4} M, acetonitrile solution): 151.2 Ω^{-1} mol^{-1} cm^2.

$[Ir(ppy)_2(dpt\text{-}NH_2)](PF_6)$ (2). The synthetic procedure used was very similar to that described above for **1**. Employed quantities: $[Ir(ppy)_2Cl]_2$, 0.020 g, 0.019 mmol; dpt-NH_2, 0.0089 g, 0.037 mmol. Yield: 0.024 g, 75%. Color: red-brown. Typical IR bands (KBr pellets, cm^{-1}): 1608 (m), 1479 (m), 1455 (w), 1422 (w), 843 (s), 755 (m), 558 (m). Anal. Found (calc) for $[Ir(ppy)_2(dpt\text{-}NH_2)](PF_6)$: C, 46.3 (46.2); H, 3.0 (3.1); N, 12.6 (12.7). Λ (5×10^{-4} M, acetonitrile solution): 139.2 Ω^{-1} mol^{-1} cm^2.

Results

$[Rh(ppy)_2(dpt\text{-}NH_2)]^+$ and $[Ir(ppy)_2(dpt\text{-}NH_2)]^+$ were prepared by the cleavage of the appropriate dichloro-bridged dimer with 4-amino-3,5-bis(2-pyridyl)-4*H*-1,2,4-triazole. The synthetic procedure is based on a well-known method used to obtain heteroleptic Rh(III) and Ir(III) cyclometalated species[5] and gives the desired products in good yields and purity even in the present case. Longer reaction times have been necessary for the iridium species, in agreement with the different reactivities of Rh and Ir metal ions.[9] The synthetic route is represented in Scheme 1.

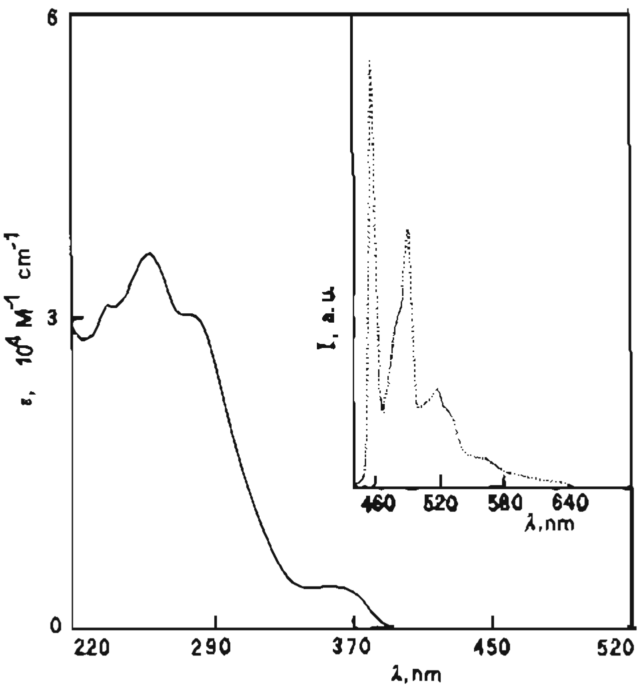
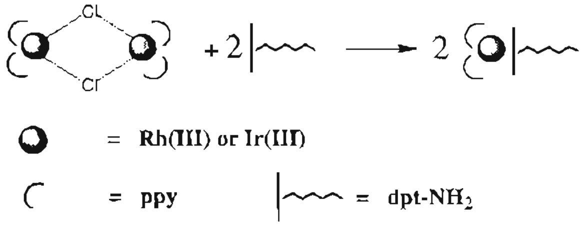


Figure 2. Absorption spectrum (in acetonitrile solution at 298 K) and (inset) luminescence spectrum (in 4:1 MeOH/EtOH at 77 K) of $[Rh(ppy)_2(dpt\text{-}NH_2)]^+$.

Scheme 1



The complexes are stable in the solvents used for at least 24 h, as shown by the constancy of their absorption spectra.

The absorption spectra of the complexes in acetonitrile fluid solution (Figures 2 and 3) show intense absorption features below 300 nm (ε in the range 10^4-10^5 M^{-1} cm^{-1}) and moderately intense absorption at longer wavelenghts (ε in the range 10^3-10^4 M^{-1} cm^{-1}). The absorption spectrum of the iridium compound also shows a long tail into the visible region, while the rhodium species is practically nonabsorbing above 400 nm.

Both Rh and Ir species are luminescent at 77 K in a MeOH/EtOH 4:1 (v/v) rigid matrix. Their luminescence spectra, displayed in the insets of Figures 2 and 3, are structured (the structure is more evident in the Rh compound), do not change with the excitation wavelength, and exhibit a vibrational progression of about 1300 cm^{-1}. The luminescence lifetimes are in each case strictly monoexponentials and are 160 and 5.8 μs for **1** and **2**, respectively. Only $[Ir(ppy)_2(dpt\text{-}NH_2)]^+$ exhibits room-temperature emission in acetonitrile (AN) fluid solution, with a quantum yield of 0.246 (deareated AN). Its emission spectrum is unstructured, excitation wavelength independent, and red-shifted with respect to the low-temperature one. It

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Table 1. Absorption Data, Luminescence, and Electrochemical Properties of the New Complexes 1 and 2 and Selected Data for Some Reference Compounds[a]

		luminescence							
		298 K			77 K[b]		electrochemistry: $E_{1/2}$, V vs SCE		
compound	absorption (298 K): λ_{max}, nm (ϵ, 10^{-3} M^{-1} cm^{-1})	λ_{max}, nm	τ, ns	Φ	λ_{max}, nm	τ, μs	oxidn	redn	
$[Rh(ppy)_2(dpt\text{-}NH_2)]^+$ (**1**)	260 (37.0) 360 (4.3)				458	160	+1.51[c]	−1.90[c]	−2.14
$[Ir(ppy)_2(dpt\text{-}NH_2)]^+$ (**2**)	267 (52.0) 418 sh (4.0) 475 (0.55)	560	870	0.246	475	5.8	+1.23	−1.75[c]	−2.08
dpt-NH_2[d]	296 (32.0)						>+1.80	<−1.80	
ppy[e]	247 (12.0)				430	>10^5	>+1.80	<−1.80	
$[Rh(ppy)_2(bpy)]^+$[f]	367 (8.0)[g]	454[g,h]	<50[g]		454[b]	170[b]	+1.10[c,i]	−1.41	
$[Ir(ppy)_2(bpy)]^+$[j]	465 (0.58)[k]	606[k]	340		532[k]	5.2[k]	+0.89[l]	−1.77[l]	−2.42[l]

[a] In acetonitrile deareated solutions, unless otherwise noted. [b] In 4:1 MeOH/EtOH (v/v) rigid matrix. [c] Irreversible wave. The reported value is E_{peak} at a scan rate of 50 mV/s. [d] Data from ref 16. [e] Data from ref 2a. [f] Data from refs 17 and 18. [g] Data in dichloromethane. [h] At 222 K. [i] In DMF *vs* NHE. [j] Data from refs 3 and 19. [k] In MeOH. [l] In DMF *vs* $Fc^{+/0}$ at 219 K.

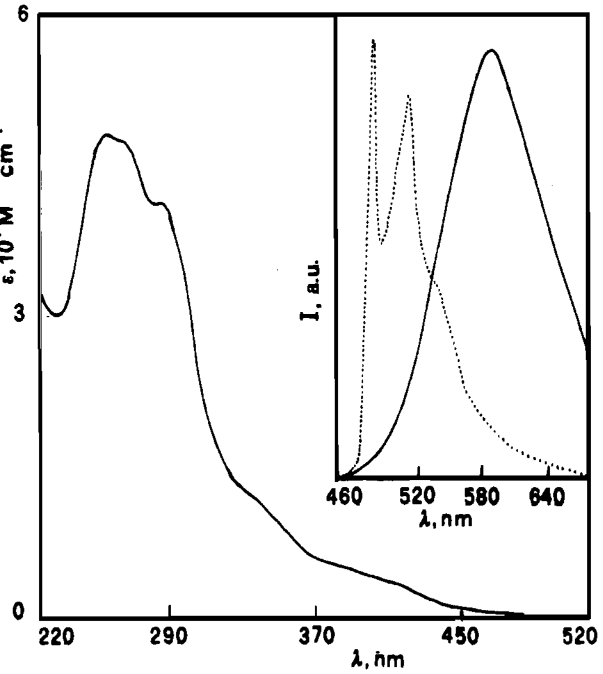

Figure 3. Absorption and (inset) luminescence spectra of $[Ir(ppy)_2(dpt\text{-}NH_2)]^+$: solid line, acetonitrile solution at 298 K; dashed line, 4:1 MeOH/EtOH (v/v) rigid matrix at 77 K.

exhibits a monoexponential decay, yielding a lifetime of 870 ns in deaerated AN.

Both iridium and rhodium complexes show only one oxidation process within the redox window investigated (<+1.80 V *vs* SCE). The half-wave potential of the oxidation of the Ir species occurs at +1.23 V *vs* SCE. The constancy of the cathodic and anodic peaks on changing scan rate from 50 mV/s to 1 V/s and their separation (80 mV, slightly larger than theoretical separation for a one-electron process, 59 mV) indicate that the process is a quasi-reversible one. On the contrary, $[Rh(ppy)_2(dpt\text{-}NH_2)]^+$ exhibits an irreversible process. In fact, the anodic peak potential moves from +1.51 V (scan rate 50 mV/s) to +1.53 V (scan rate 500 mV/s), and no clear cathodic peak could be revealed.

The reduction patterns of the two complexes (reduction window up to −2.20 V *vs* SCE) are quite similar. In each case, two reduction processes occur: the one at less negative potential (about −1.75 V for the Ir species and −1.90 V for the Rh one) is irreversible, while the one at more negative potential (−2.08 V for $[Ir(ppy)_2(dpt\text{-}NH_2)]^+$ and −2.14 V for the Rh analogue) is reversible or quasi-reversible. Data on absorption spectra, luminescence properties, and redox behavior of the new complexes are collected in Table 1, together with selected data for ligands and reference compounds.

Discussion

The spectroscopic and electrochemical behavior of transition metal complexes and of organometallic compounds is usually discussed with the assumption that the ground state as well as the excited and redox states involved to interpret the observed properties can be described by a localized molecular orbital configuration.[20] Within such an assumption, the various spectroscopic transitions are classified as metal centered (MC), ligand centered (LC), or charge transfer (either metal-to-ligand, MLCT, or ligand-to-metal, LMCT), and the oxidation and reduction processes are classified as metal or ligand centered. This simplified picture, of course, is less applicable for organometallic compounds, when a large degree of covalency exists in metal−ligand bonds. Furthermore, other types of orbitals (and states) were invoked to interpret the spectroscopic and electrochemical properties of metal compounds with strong electron donor ligands. For example, mixed $Pt(d_\pi)/S(p)$ ligand orbitals have been considered to be involved in the photophysical properties of Pt(II) dithiolate complexes,[21] and a covalent metal−C^- σ-bonding (or metal-Si^- σ-bonding) orbital has been identified as the orbital involved in the oxidation process and the lowest-lying charge transfer excited state in Ir(III) and Rh(III) cyclometalated compounds.[6,22] In particular, Kirsch-DeMesmaeker, Watts, and co-workers[6] have concluded that the lowest energy excited states of $[Ir(ppy)_2TAP]^+$, $[Rh(ppy)_2TAP]^+$, and $[Rh(ppy)_2HAT]^+$ (TAP = 1,4,5,8-tetraazaphenanthrene; HAT = 1,4,5,8,9,12-hexaazatriphenylene) would involve a transition from such a σ-bond orbital to a π^* orbital of the polypyridine ligand (σ-bond to ligand charge transfer, SBLCT). SBLCT excited states have also been considered to rationalize the photophysical properties of mixed-metal tetranuclear Ru−Ir compounds.[9b]

Electrochemistry. While the electrochemical processes occurring in metal polypyridyne complexes are usually revers-

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ible and relatively easy to assign to metal-centered and ligand-centered orbitals, the HOMO and LUMO involved in the redox processes occurring in cyclometalated compounds are more difficult to identify, especially as far as the oxidation processes are concerned. However, the following guidelines can be given. Oxidation of the metal ion in mononuclear mixed-ligand cyclometalated Ir(III) and Rh(III) species is expected to be a reversible (or quasi-reversible) process, analogous to metal-centered oxidation in Ru(II)− and Os(II)−polypyridine complexes.[5] On the contrary, one-electron abstraction from Ir(d_π)−σ(C^-), or Rh(d_π)−σ(C^-), σ-bond orbital leads to a dramatic weakening and successive breaking of the metal−C^- bond.[6] As a consequence, σ-bond orbital oxidation is expected to be irreversible.

On the basis of the above considerations, the irreversible oxidation of $[Rh(ppy)_2(dpt\text{-}NH_2)]^+$ at +1.51 V (anodic peak) (Table 1) should involve a σ-bond orbital, while the quasi-reversible nature of the $[Ir(ppy)_2(dpt\text{-}NH_2)]^+$ oxidation at +1.23 V suggests a metal-centered orbital as the oxidation site (the HOMO) in the latter compound, with only a minor contribution, if any, from σ-bond orbitals. The difference in the potential between Ir- and Rh-centered oxidations (Rh-centered oxidation should occur at more positive potentials than 1.51 V, the value of the first oxidation of the Rh complex, which involves a σ bond orbital) is in agreement with the expected electron densities at the two metal ions. The oxidation of $[Ir(ppy)_2(dpt\text{-}NH_2)]^+$ occurs at less positive potential with respect to that of $[Ir(ppy)_2(HAT)]^+$ (quasi-reversible process at +1.44 V *vs* SCE, difference between cathodic and anodic peaks 110 mV)[6] and is quite similar to that of $[Ir(ppy)_2(bpy)]^+$ (+0.89 vs ferrocene).[3] The reason for such a behavior can be ascribed to the different electron donor properties of the polypyridine ligands, which increase in the series HAT < bpy ≤ dpt-NH_2, as suggested by comparisons of the oxidation potentials of $[Ru(bpy)_3]^{2+}$, $[Ru(bpy)_2(HAT)]^{2+}$, and $[Ru(bpy)_2(dpt\text{-}NH_2)]^{2+}$ (+1.23,[23] +1.56,[24] and +1.20 V,[16] respectively). The different electron donor properties of dpt-NH_2 with respect to HAT move the Ir d_π orbitals to higher energy. Therefore, the increased energy gap between metal-centered d_π and σ-bond orbitals in $[Ir(ppy)_2(dpt\text{-}NH_2)]^+$ with respect to $[Ir(ppy)_2(HAT)]^+$ would explain a decreased contribution of the σ-bond orbital in the HOMO of $[Ir(ppy)_2(dpt\text{-}NH_2)]^+$, which justifies the closer conformity of the oxidation of the latter compound to the reversibility criteria.

Because of the similarity of the reduction patterns in the new compounds, they will be discussed together. The first reduction of both complexes cannot be assigned to phenylpyridine ligands, because of the following arguments: phenylpyridine reductions in Rh(III) and Ir(III) cyclometalated complexes (i) are known to be reversible and (ii) usually occur at potential more negative than −2.00 V *vs* SCE.[5] As a consequence, the first (irreversible) reduction of the new compounds must involve dpt-NH_2.[25] Such an assignment is also supported by the irreversible reduction of the quite similar ligand (1M3ptr) in $[Ru(1M3ptr)_3]^{2+}$ (1M3ptr = 1-methyl-3-(2-pyridyl)-1,2,4-triazole), occurring at −1.75 V *vs* SCE in acetonitrile.[26] The second (reversible) reductions of both Rh and Ir compounds occur at the typical potentials of ppy reductions of analogous cyclometalated species[5] and are therefore safely assigned to ppy reductions.

It is interesting to note that both dpt-NH_2 and ppy reductions occur at less negative potentials for the Ir compound than for the Rh one. This can be explained by considering the effect of ligand−ligand interactions. Such interactions stabilize the first reduction process on the ligands by the contribution of the not yet reduced ligand(s) in delocalizing the negative charge in excess located in the first reduced ligand and can be mediated by metal ion orbitals: Ir(d_π) orbitals, which are closer in energy to the π^* orbitals of the ligands where reduction occurs with respect to Rh(d_π) (and Rh−C^- σ-bond) orbitals, as indicated by oxidation potentials, are more effective in promoting ligand−ligand interactions.

Absorption Spectra. The absorption features of the new complexes at λ < 320 nm are mainly due to ligand-centered (ppy and/or dpt-NH_2) transitions. In particular, the band at about 290 nm most likely originates from metal-perturbed dpt-NH_2-centered transitions, while the absorption maximum at about 260 nm receives the main contribution from metal-perturbed ppy-centered transitions. Such assignments are based on the following: (i) the high extinction coefficients of the bands, which are consistent with $\pi \rightarrow \pi^*$ transitions in polypyridine-like metal complexes; (ii) the similitude with ppy-centered bands in the protonated ppy (λ_{max} = 247 nm, ϵ = 12 100 M^{-1} cm^{-1} in nitrile solution[5]) and in other Rh(III) and Ir(III) cyclometalated compounds;[5] (iii) the reported $\pi \rightarrow \pi^*$ band for the dpt-NH_2 free ligand (λ_{max} = 296 nm, ϵ = 32 000 M^{-1} cm^{-1}).[16]

As far as the moderately intense absorption bands (or shoulders) at λ > 320 nm are concerned, charge transfer assignments are most appropriate. In fact, bands of similar energies, intensities, and shapes have been reported to be CT transitions in Rh(III) and Ir(III) cyclometalated compounds.[5] On the basis of the considerations made above and the electrochemical results, the absorption bands are probably superpositions of MLCT and SBLCT bands. Because of the strong mixture between metal and ligand orbitals occurring in cyclometalated compounds and the known difficulties in correlating electrochemical and spectroscopic properties of these species, we prefer not to discuss the CT bands in further detail. Interestingly, the LC bands of the Ir compound are more intense than the analogous LC bands of the Rh species (Figures 2 and 3). This is probably due to higher-energy CT transitions which can contribute to absorption in the 300 nm region. Such CT transitions are expected to be more effective in the Ir compound.

The long absorption tail toward lower energies exhibited by the Ir compound is assigned to singlet-to-triplet CT transitions, enhanced in magnitude because of the strong spin−orbit coupling due to the heavy metal ion.

Luminescence Properties. Luminescence of Rh(III) and Ir(III) cyclometalated compounds has often been a matter of debate. In general, LC, MLCT, and, in recent times, SBLCT excited states were identified as being responsible for light emission. In rare cases, also MC luminescence has been investigated. Often, extensive mixing between excited states made it difficult to arrive at clear-cut assignments. Multiple emissions, especially at 77 K, have also been found and can further complicate the luminescence studies.

For the complexes studied here, the interpretation of the emission properties is almost straightforward. Actually, the long luminescence lifetime exhibited by **1** at 77 K (Table 1, Figure 2) strongly indicates a metal-perturbed ^{3}LC as the lowest-lying, luminescent level of this species. This assignment is confirmed by the lack of room-temperature luminescence of **1**. It is well-known, in fact, that metal-perturbed ^{3}LC excited states, which can be fairly emissive at 77 K in a rigid matrix, are rarely emissive at room temperature in fluid solution, because they

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[25] Metal-based reductions are also excluded since they are not expected to occur at so low negative potentials in cyclometalated compounds.
[26] Hage, R. Ph.D. Dissertation, University of Leiden, Leiden, The Netherlands, 1991.

are effectively deactivated by thermal population to upper-lying ^{3}MC levels, which finally deactivate by fast radiationless transitions to the ground state.[5,23]

Whether the luminescent LC excited state is ppy centered or dptNH$_2$ centered is less clear. However, we believe that the emission can be safely assigned to a ppy-centered level, most likely mixed with a closely-lying CT excited state, because of the close similarity between the emission of **1** and that reported for [Rh(ppy)$_2$(bpy)]$^+$ (highly-structured emission almost overlapping that of **1** and peaking at 454 nm; $\tau = 170$ μs[17,18]), which has been assigned to a ppy-centered level somewhat mixed with an upper-lying CT level.[27] The situation should be almost equivalent in **1**, the only difference being that dpt-NH$_2$ is slightly a better donor group than bpy and could move the Rh → ppy CT level to lower energy, furtherly decreasing the energy gap between LC and MLCT states, promoting a better mixing, and leading to a shortened lifetime. The very small difference between the luminescence lifetimes of **1** and [Rh(ppy)$_2$(bpy)]$^+$ (probably not far from the experimental errors) seems to indicate that significant differences (in this regard) do not exist between the electron-donor properties of bpy and dpt-NH$_2$.

As far as the luminescence of [Ir(ppy)$_2$(dpt-NH$_2$)]$^+$ (**2**) is concerned, the shape of the spectra, the lifetimes at 77 K and at room temperature, and the energies point to a ^{3}MLCT assignment of the emission. In fact, a *bona fide* ppy-centered emission in an Ir−ppy compound is that of [Ir(ppy)$_2$(CO)Cl], which occurs at 455 nm with a lifetime of 28 μs at 77 K,[29] while ^{3}MLCT emitters are typically shorter-lived and strongly matrix-dependent (the emission is red-shifted on passing from 77 K to room-temperature fluid solution). Also SBLCT emission seems to be less probable, because of the structured shape of the spectra (SBLCT are quite distorted states and exhibit very broad emissions[6]). Furthermore, the reversible nature of the oxidation process of **2** clearly suggests the pure metal-centered nature of the HOMO in **2**, as already discussed above. To decide whether the luminescent CT level involves a ppy or the dpt-NH$_2$ ligand is a much more difficult task. The electrochemical investigations, quite useful for the assignment of the emission in polypyridine complexes, are useless in this case, because in cyclometalated compounds the π^* LUMO orbital (identified by the first reduction process) can be different from the π^* orbital that is involved in the lowest energy MLCT level, because of the different covalencies in the metal−ligand bonds of polypyridine and cyclometallating ligands and of a possible split in the t$_{2g}$ metal orbitals due to different donor abilities of the ligands.[6,9,30]

In a first attempt to assign the emission of **2**, we compared our results with the luminescence properties of [Ir(ppy)$_2$(bpy)]$^+$.[31] The 77 K luminescence of this species ($\lambda_{\max} \sim 530$ nm; main lifetime = 5.2 μs) originates from two closely-lying nonequilibrated MLCT states, the lower one involving the bpy ligand and the higher one involving ppy. In fluid acetonitrile solution, only the Ir → bpy CT emission was observed ($\lambda_{\max} = 606$ nm; $\tau = 0.34$ μs), as definitely revealed by transient absorption spectroscopy.[31b] In [Ir(ppy)$_2$(dpt-NH$_2$)]$^+$, the replacement of bpy with dpt-NH$_2$ noticeably raises the energy of the CT level involving the polypyridine ligand (dpt-NH$_2$ is much more difficult to reduce than bpy[16]), while the energy of the CT level involving ppy is probably slightly decreased. Unfortunately, these considerations are consistent with CT emission involving either ppy or dpt-NH$_2$ and cannot help in assigning the luminescence. A more instructive consideration is maybe the experimental observation that MLCT excited states involving cyclometalated ligands seem to be much less stabilized in energy with regard to MLCT levels involving polypyridine ligands on passing from rigid matrix to fluid solution.[5] This leads to the suggestion that the room-temperature emission of **2** most likely originates from an Ir → dpt-NH$_2$ CT level. It is impossible to draw a clear-cut conclusion as to which ligand is involved in the MLCT emission at 77 K.

At the end of this section, it is useful to compare the present results with those recently reported for the similar compounds [Ir(ppy)$_2$TAP]$^+$, [Rh(ppy)$_2$TAP]$^+$, and [Rh(ppy)$_2$HAT]$^+$.[6] In particular, it is worthwhile to discuss the absence of the involvement of SBLCT excited states in the luminescence properties. The reason for such behavior lies probably in the electron-donor properties of dpt-NH$_2$, which are similar to those of bpy and much better than those of HAT or TAP ligands. As a consequence, the dπ orbitals of Rh(III) and Ir(III) are raised in energy (see also the electrochemical section) and their mixing with the σ orbitals of the cyclometalating anionic ligands is substantially decreased. This ultimately leads to high-lying SBLCT levels.

Conclusions

Two new cyclometalated Rh(III) and Ir(III) complexes have been synthesized, and their absorption spectra, luminescence properties (in rigid matrix at 77 K and in fluid solution at room temperature), and electrochemical behavior have been investigated and compared to those of other similar Rh(III) and Ir(III) cyclometalated species. Correlation between the reversibility of the oxidation process and the nature of the donor orbital (metal-centered or metal−ligand (C$^-$) σ bonding) which is involved in the luminescent CT level[6] are confirmed. The results obtained are a step toward the preparation of photoactive and redox-active multinuclear compounds based on bis(pyridyl)-triazole derivative bridges and incorporating Ir(III) and Rh(III) cyclometalated building blocks.

Acknowledgment. This work was supported by the Consiglio Nazionale delle Ricerche and by the Ministero dell'Università e della Ricerca Scientifica e Tecnologica. S.S. also thanks the CNR for support under Grant No. 201.03.20.

IC940875C

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(27) The contribution of a CT level to the ppy-centered luminescent level of [Rh(ppy)$_2$bpy]$^+$ (and therefore of **1**) was based on its luminescence lifetime, 170 μs, shortened with respect to that of [Pt(ppy)$_2$(CH$_2$Cl)-Cl], 300 μs, a *bona fide* ppy-centered emitter,[28] in spite of the fact that Rh is lighter than Pt. Furthermore, a triplet Rh-to-ppy CT level was expected to lie very close in energy to 450 nm in [Rh(ppy)$_2$bpy]$^+$.[5]

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(30) In the present case, furthermore, the situation is complicated by the irreversible nature of the dpt-NH$_2$ reduction.

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