

Chemical and Electrochemical Generation of Hydride-Forming Catalytic Intermediates (bpy)M(C_nR_n): M = Rh, Ir (n = 5); M = Ru, Os (n = 6). Coordinatively Unsaturated Ground State Models of MLCT Excited States?

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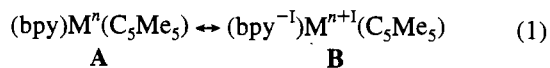
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The d⁶ metal complex ions [(bpy)MCl(C_nR_n)]⁺ [bpy = 2,2'-bipyridine; M = Rh, Ir (n = 5, R = Me); M = Ru (n = 6; C₆R₆ = C₆H₆, *p*-MeC₆H₄Pr, C₆Me₆); M = Os (n = 6; C₆R₆ = *p*-MeC₆H₄Pr, C₆Me₆)] were prepared as hexafluorophosphate salts and studied by cyclic voltammetry. In each case, a two-electron reduction produced highly colored coordinatively unsaturated species (bpy)M(C_nR_n) which could also be obtained via chemical reduction. ¹H and ¹³C NMR high field shifts of bpy resonances, cathodically shifted secondary one-electron reduction waves, and the vibrationally structured long-wavelength absorption features in the visible region of these neutral compounds all suggest an oxidation state distribution involving a partially reduced bpy ligand. Such an electronic structure would correspond to the typical formulation of low-lying MLCT excited states in conventional d⁸ metal complexes and may be relevant for the functioning of the systems as catalysts for hydride transfer, including H₂ evolution. Stable hydride intermediates of this catalysis were isolated and characterized in the case of the 5d systems [(bpy)MH(C_nR_n)]⁺ [M = Ir (n = 5) and Os (n = 6)] which could be reversibly reduced to neutral radical complexes as evident from a resolved EPR spectrum.

Oxidative addition/reductive elimination reactions between d⁶ and coordinatively less saturated d⁸ configurations are highly important in homogeneous catalysis,¹ involving redox couples such as Rh(I/III), Ir(I/III), Ru(0/II), and Os(0/II) in the case of reductive (e.g. hydrogenation) reactions. The electron-rich d⁸ metal complex states often require some steric protection for selectivity or for stabilization of the low-valent and coordinatively unsaturated metal centers; triorganophosphine or π -coordinated (alkylated) cycloarene ligands have frequently been used for this purpose. The M(C₅Me₅) fragments (M = Rh, Ir) in particular have proven to be very valuable for studies directed at the activation of C–H or C–F bonds^{2–4} or catalytic processes,⁵ for stabilization of carbene, nitrene, or polyhydride intermediates,⁶ and for "bioorganometallic" chemistry.⁷ In conjunction with 2,2'-bipyridine as coligand, the Rh(C₅Me₅) fragment was described as reduced intermediate for hydride transfer processes, i.e. the reduction of protons to H₂.^{8,9} or of

NAD⁺ to NADH.¹⁰ The hydride intermediate [(bpy)MH(C₅Me₅)]⁺ could be isolated and studied, e.g. with respect to photoinduced H₂ generation, when the corresponding iridium analogue was used.^{11,12} The coordinatively unsaturated reduced forms (bpy)M(C₅Me₅) with formally univalent metal showed an unusual electrochemical and spectroscopic behavior which has been tentatively interpreted within the resonance formulations A and B.¹³

Scheme 1



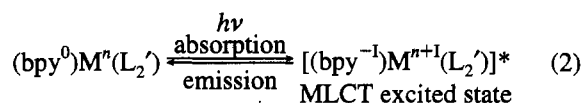
Specifically, the complexes (α -diimine)M(C₅Me₅) (M = Rh, Ir) are reduced at more negative potentials than the corresponding free α -diimine acceptor ligands, which points to a very strong degree of metal-to-ligand electron shift via π back-

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donation in the ground state.^{12–14} Furthermore, the complexes of aromatic α -diimines such as bpy or diaza derivatives thereof exhibit structured long-wavelength features in their electronic absorption spectra,^{12,13} the spacing of about 1300 cm^{-1} being similar to the vibrational structure of the forbidden long-wavelength bands of singly reduced α -diimines and their complexes.^{15–17} In “normal” complexes such as (α -diimine)-ML ($M = \text{Rh, Ir; L} = \text{diolefins}$), such structuring is observed not in the absorption but in the emission spectra resulting from MLCT excited states (Scheme 2).^{18,19}

Scheme 2



$M = \text{Rh, Ir; } n = +1;$

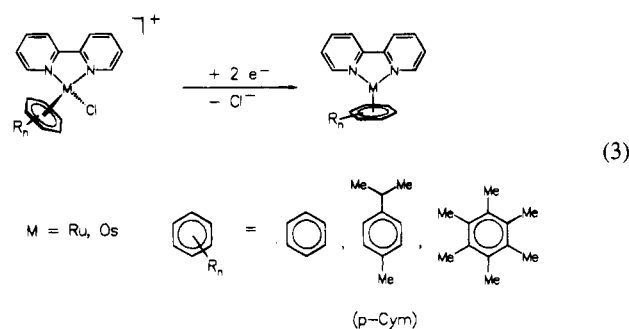
$\text{L}_2' = \text{diolefin (e.g., 1,5-cyclooctadiene, norbornadiene)}$

Finally, the NMR signals show pronounced high-field shifts and patterns^{12,13} which correspond very closely to the theoretically and experimentally determined spin distributions of the α -diimine anion radicals.^{20,21} Even the reduced forms $[(\alpha\text{-diimine})\text{Rh}(\text{C}_5\text{Me}_5)]^{\cdot-}$ still show the effects of the very strong π electron donor $(\text{C}_5\text{R}_5)\text{Rh}$ on the spin distribution of the α -diimine radical anion via EPR spectroscopy.²² The lower stability of the iridium complex relative to that of the rhodium analogue¹² can also be tentatively attributed to higher contributions from resonance form **B** which involves strong magnetic coupling²³ between an anion radical ligand²⁴ with a low-spin d^7 metal ion. The recently reported^{11c} structure of $(\text{bpy-4,4'-(COOH)}_2)\text{Ir}(\text{C}_5\text{Me}_5)$ further reflects the extraordinary electron excess in these 18-valence-electron complexes via a distinctly “slipped” cyclopentadienide ring (3+2 coordination).

In this work we try to substantiate the assertion of Scheme 1 by reporting electrochemical and spectroscopic results of group 8 metal analogues (Scheme 3) with arene (benzene, *p*-cymene, hexamethylbenzene) instead of cyclopentadienide ligands. These compounds can be obtained via reduction from corresponding cationic metal(II) halide precursor complexes (Scheme 3). Similarities and differences to the group 9 metal systems should provide further evidence for or against the participation of formula **B** in Scheme 1 to the electronic ground state of such reactive intermediates.

In the course of these studies we also obtained isolable hydride complex ions $[(\text{bpy})\text{OsH}(\text{C}_6\text{R}_6)]^+$ which were found to

Scheme 3



undergo a reversible reduction to EPR-detectable neutral radical complexes $(\text{bpy})\text{OsH}(\text{C}_6\text{H}_6)$.

Experimental Section

Syntheses. The rhodium and iridium complexes referred to in this work were described earlier.^{11–13} Due to their extraordinary reactivity toward electrophiles the neutral (reduced) complexes $(\text{bpy})\text{M}(\text{C}_6\text{R}_n)$ can only be obtained and reacted in rigorously dried solvents under argon; spectroscopic investigations (NMR, EPR, UV/vis) had to be performed in sealed tubes or special Schlenk cuvettes, and elemental analyses or precise molar extinction coefficients could thus not be obtained. Starting materials for the ruthenium and osmium complexes were prepared as described in the literature.^{25,26}

$(\text{bpy})\text{RuCl}(\text{C}_6\text{H}_6)(\text{PF}_6)$. A 200 mg amount (0.4 mmol) of $[\text{RuCl}_2(\text{C}_6\text{H}_6)]_2^{25a}$ was reacted for 1 h at room temperature with 156 mg (1 mmol) of 2,2'-bipyridine in 25 mL of methanol. After filtration the orange-yellow solution was treated with a concentrated methanolic solution of Bu_4NPF_6 , and the yellow precipitate was washed with methanol and diethyl ether to yield 200 mg (47%) of yellow microcrystals. λ_{max} (CH_3CN): 405 sh, 340, 312, 302, 291 nm. Anal. Calcd for $\text{C}_{16}\text{H}_{14}\text{ClF}_6\text{N}_2\text{PRu}$ ($M = 515.79$): C, 37.21; H, 2.73; N, 5.43. Found: C, 37.34; H, 2.72; N, 5.51.

$(\text{bpy})\text{RuCl}(p\text{-Cym})(\text{PF}_6)$. A 100 mg amount (0.16 mmol) of $[\text{RuCl}_2(p\text{-Cym})]_2^{25}$ was reacted for 12 h at room temperature with 80 mg (0.5 mmol) of 2,2'-bipyridine in 30 mL of methanol. The yellow solution was concentrated to 15 mL and treated with a solution of 620 mg (1.6 mmol) of Bu_4NPF_6 in 10 mL of methanol to yield a yellow precipitate, which was washed with methanol and diethyl ether to give 120 mg (66%) of yellow microcrystals. λ_{max} (CH_3CN): 428, 335 nm. Anal. Calcd for $\text{C}_{20}\text{H}_{22}\text{ClF}_6\text{N}_2\text{PRu}$ ($M = 572.01$): C, 41.96; H, 3.88; N, 4.90. Found: C, 42.45; H, 4.23; N, 4.77.

$(\text{bpy})\text{RuCl}(\text{C}_6\text{Me}_6)(\text{PF}_6)$. An amount of 67 mg (0.10 mmol) of $[\text{RuCl}_2(\text{C}_6\text{Me}_6)]_2^{25b}$ was reacted for 30 min with 47 mg (0.3 mmol) of 2,2'-bipyridine in 30 mL of methanol. The solution was concentrated to 10 mL and treated with a solution of 116 mg (0.30 mmol) Bu_4NPF_6 in about 5 mL of methanol to yield 80 mg (67%) of orange-yellow microcrystals. λ_{max} (CH_3CN): 423, 343 nm. Anal. Calcd for $\text{C}_{22}\text{H}_{26}\text{ClF}_6\text{N}_2\text{PRu}$ ($M = 600.05$): C, 44.00; H, 4.37; N, 4.67. Found: C, 44.00; H, 4.47; N, 4.62.

$(\text{bpy})\text{OsCl}(p\text{-Cym})(\text{PF}_6)$. A 250 mg amount (0.316 mmol) of $[\text{OsCl}_2(p\text{-Cym})]_2^{26a}$ was reacted with 123 mg (0.79 mmol) of 2,2'-bipyridine in 20 mL of methanol, first for 12 h at room temperature and then for an additional 4 h under reflux. The brownish suspension was filtered, and the filtrate was concentrated to about 5 mL and treated with a concentrated methanolic solution of Bu_4NPF_6 to yield 258 mg (74%) of yellow microcrystals. λ_{max} (CH_3CN): 456 sh, 394 nm. Anal. Calcd for $\text{C}_{20}\text{H}_{22}\text{ClF}_6\text{N}_2\text{OsP}$ ($M = 661.02$): C, 36.34; H, 3.35; N, 4.24. Found: C, 36.41; H, 3.23; N, 4.13.

$(\text{bpy})\text{OsCl}(\text{C}_6\text{Me}_6)(\text{PF}_6)$. An amount of 50 mg (0.059 mmol) of $[\text{OsCl}_2(\text{C}_6\text{Me}_6)]_2^{26b}$ was reacted with 27 mg (0.177 mmol) of 2,2'-

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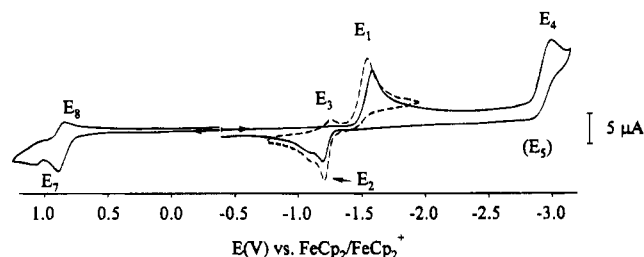


Figure 1. Cyclic voltammograms of [(bpy)OsCl(C₆Me₆)](PF₆) in CH₃CN containing 0.1 M Bu₄NPF₆ at 100 mV/s (—) and 200 mV/s (---, second cycle).

bipyridine in 20 mL of methanol for 12 h at ambient temperature and then for 2 h under reflux. The solution was concentrated to 10 mL and treated with a solution of 68 mg (0.177 mmol) of Bu₄NPF₆ in 5 mL of methanol to yield 40 mg (50%) of orange microcrystals. λ_{max} (CH₃CN): 486 sh, 412, 291 nm. Anal. Calcd for C₂₂H₂₆ClF₆N₂OsP (*M* = 689.09): C, 38.35; H, 3.80; N, 4.07. Found: C, 38.13; H, 3.74; N, 4.13.

[(bpy)M(C₆R₆)] (General Procedure). A solution of 0.05 mmol of [(bpy)MCl(C₆R₆)](PF₆) in about 15 mL of dry THF was allowed to react with a potassium mirror produced by vacuum distillation of 0.05 g (1.25 mmol) of potassium. After 5 min the color had changed from yellow to deep purple (Ru) or dark red (Os) whereupon the solution was immediately filtered and the solvent removed in vacuo to yield 10–15 mg (60–80%) of very sensitive purple (Ru) or dark red (Os) microcrystals.

[(bpy)OsH(*p*-Cym)](BPh₄). A 10 mg amount (0.020 mmol) of [(bpy)Os(*p*-Cym)] was added to a suspension of 100 mg (0.61 mmol) of NH₄PF₆ in 10 mL of THF. After color change from orange-red to dark yellow, concentration to 5 mL, and addition of 34 mg (0.10 mmol) NaBPh₄ dissolved in 5 mL of ethanol, the product precipitated as air- and light-sensitive yellow crystals in 130 mg (80%) yield. ν_{Os-H} (CD₂-Cl₂): 2014 cm⁻¹. λ_{max} (CH₂Cl₂): 481 sh, 436 nm.

[(bpy)OsH(C₆Me₆)](BPh₄). A 10 mg amount (0.020 mmol) of [(bpy)Os(C₆Me₆)] was dissolved in 10 mL of THF and treated with a solution of 20 mg (0.060 mmol) of NaBPh₄ in 10 mL of ethanol. Addition of an aqueous solution of 30 mg (0.18 mmol) of NH₄PF₆ and evaporation of the solvent produced a brown precipitate which was separated by filtration and washed with ethanol to yield 13 mg (80%) of dark-brown air-stable crystals. ν_{Os-H} (CD₂-Cl₂): 2000 cm⁻¹. λ_{max} (CH₂Cl₂): 519 sh, 444, 374 nm. Anal. Calcd for C₄₆H₄₇BN₂O₈ (*M* = 828.91): C, 66.65; H, 5.71; N, 3.38%. Found: C, 65.54; H, 5.88; N, 3.45%.

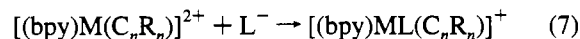
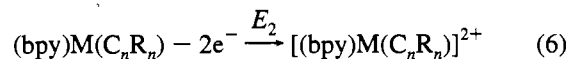
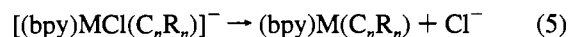
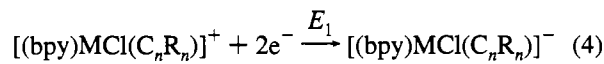
Instrumentation. NMR spectra were taken on a Bruker AC 250 spectrometer. EPR spectra were recorded in the X band on a Bruker System ESP 300 equipped with a Bruker ER035M gaussmeter and a HP 5350B microwave counter. The radical complex (bpy)OsH(C₆Me₆) was generated in a two-electrode EPR tube. Infrared vibrational spectra were obtained using a Perkin-Elmer 684 spectrometer. UV/vis spectra were recorded on spectrophotometers Shimadzu UV160 and Bruins Instruments Omega 10. Cyclic voltammetry was carried out in acetonitrile containing 0.1 M Bu₄NPF₆ using a three-electrode configuration (glassy-carbon working electrode, platinum-wire counter electrode and Ag/AgCl as reference) and a PAR 273 potentiostat. The ferrocene/ferrocenium (Fc/Fc⁺) couple was used as internal reference.

Results and Data Analysis

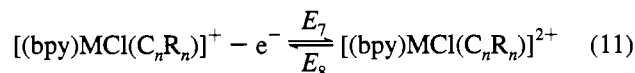
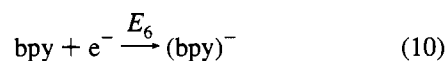
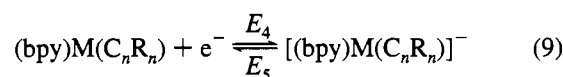
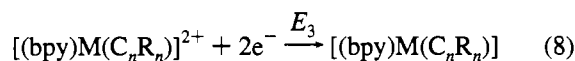
Synthesis and Electrochemistry. The Ru(II) and Os(II) halide complexes [(bpy)MCl(C₆R₆)](PF₆), synthesized via conventional routes, display a rich electrochemistry in acetonitrile as evident from the cyclic voltammogram shown in Figure 1. The pertinent peak potentials are summarized in Table 1 together with data for group 9 metal analogues,^{12,13} the individual (electro)chemical reactions, including those of the hydride

species, are listed in Schemes 4 and 5.

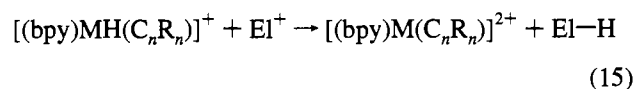
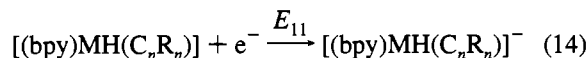
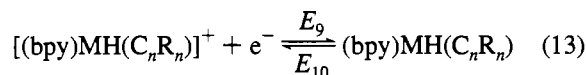
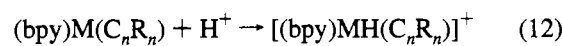
Scheme 4



L = Cl⁻ or other nucleophile



Scheme 5



El: electrophile, e.g. H⁺ or NAD⁺

The first reduction step which is obviously relevant for the catalytic hydride transfer function is a two-electron process at peak potential *E*₁ which is accompanied by a very rapid dissociation of the halide (EC mechanism) to yield the neutral compounds (bpy)M(C_nR_n) with formally d⁸-configured metal (eqs 4 and 5).

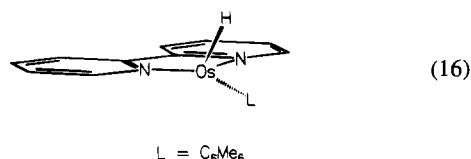
The reverse process, the oxidation of (bpy)M(C_nR_n), is also a two-electron step (*E*₂) with subsequent completion of the coordination sphere of the d⁶ metal center by addition of halide or another ligand (eqs 6 and 7). Under certain circumstances, this addition to [(bpy)M(C_nR_n)]²⁺ can be so slow that the cathodic peak *E*₃ (eq 8) corresponding to the anodic wave *E*₂ becomes visible in the cyclic voltammetric experiment, either because of rapid scan or because of sterically hindered access to the reoxidized metal center (Table 1).¹⁴

The neutral intermediates (bpy)M(C_nR_n) can be reduced one more time at very negative potentials in a partly reversible (*E*₄, *E*₅) single-electron step to anionic complexes (eq 9). In the case of [(L)Rh(C₅Me₅)]⁻, L = bpy, 2,2'-bipyrazine, or 2,2'-bipyrimidine, these anions could be clearly characterized as

Table 1. Electrochemical Data^a for 2,2'-Bipyridine^b and Its Complexes^c

complex	E_1	E_2	$ E_1 - E_2 $	E_3	E_4	E_5	$ E_6 - E_4 $	E_7	E_8
[(bpy)RhCl(C ₆ Me ₆)](PF ₆) ^h	-1.36	-1.06	0.30		-2.65	-2.57	0.08	1.50	
[(bpy)IrCl(C ₆ Me ₆)](PF ₆) ^h	-1.55	-1.04	0.51		-2.85	-2.79	0.25	0.70	
[(bpy)RuCl(C ₆ H ₆)](PF ₆)	-1.35	-1.05	0.30		-2.73	-2.64	0.16	1.39	
[(bpy)RuCl(<i>p</i> -Cym)](PF ₆)	-1.42	-1.08	0.34	-1.13 ^d	-2.80	-2.68	0.23	1.23	
[(bpy)RuCl(C ₆ Me ₆)](PF ₆)	-1.48	1.19	0.29	-1.27 ^e	-2.83	-2.73	0.26	1.06	0.99
[(bpy)OsCl(<i>p</i> -Cym)](PF ₆)	-1.49	-1.13	0.36	-1.23 ^f	-2.91		0.34	1.12	
[(bpy)OsCl(C ₆ Me ₆)](PF ₆)	-1.56	-1.23	0.33	-1.26 ^g	-3.00		0.43	0.89	0.84
complex	E_9	E_{10}	E_{11}						
[(bpy)IrH(C ₆ Me ₆)](BPh ₄) ^h	-1.87	-1.81							
[(bpy)OsH(<i>p</i> -Cym)](BPh ₄) ^c	-1.61								
[(bpy)OsH(C ₆ Me ₆)](BPh ₄)	-1.86	-1.78	-2.52						

^a From cyclic voltammograms at 100 mV/s in CH₃CN containing 0.1 M Bu₄NPF₆. Peak potentials are according to Schemes 4 and 5 in V vs Fc/Fc⁺. ^b $E_6 = E(\text{bpy}/\text{bpy}^{\cdot-}) = -2.57$ V. ^c In CH₂Cl₂ containing 0.1 M Bu₄NPF₆. ^d $i(E_3)/i(E_1) = 0.05$ (1 V/s). ^e $i(E_3)/i(E_1) = 0.31$ (1 V/s). ^f $i(E_3)/i(E_1) = 0.32$ (1 V/s). ^g $i(E_3)/i(E_1) = 0.41$ (0.5 V/s). ^h Reference 12a.

Scheme 6

anion radical complexes according to the oxidation state distribution (L^{•-})Rh^I,²² it has to be noted that in all instances the reduction peak potential E_4 of the complex occurs at more negative values than that of the free heterocyclic ligand (E_6 ; Table 1).^{12b}

Oxidation processes are reasonably well defined only for the hexamethylbenzene complexes (Figure 1, Table 1) where an apparently single-electron wave (E_7 , E_8) involving the transition M(II) → M(III) occurs to yield dicationic species with d⁵ configured metal (eq 11).

The coordinatively unsaturated neutral intermediates (bpy)M-(C_nR_n) cannot just be obtained electrochemically but can also be obtained via brief contact ($t < 5$ min) with a freshly prepared potassium mirror. A structural analysis^{11c} of the substituted bpy complex (bpy-4,4'-(COOH)₂)Ir(C₆Me₆) has shown a slight slippage of the cyclopentadienyl ring in the direction of a (3 + 2) coordination which reflects the extraordinary electron excess at the metal despite the otherwise favorable 18-valence-electron situation.

The neutral complexes are very sensitive and react rapidly with electrophiles, including H⁺ (eq 12). In the case of the 5d systems the corresponding iridium(III)^{12,13} and osmium(II) monohydride complexes were sufficiently stable to be isolated (Scheme 6). While the *p*-Cym/hydride complex of osmium was still air-sensitive, the better protected Os-H bond in the hexamethylbenzene analogue proved to be stable toward air. On the other hand, the neutral compound (bpy)Os(C₆Me₆) decomposed slowly under formation of a black insoluble material in pentane or toluene while it was stable in benzene solution. The possible cause of an alkyl C-H activation² is being investigated. The hydride complexes undergo a reversible one-electron reduction (eq 13) at potentials (E_9 , E_{10}) which are distinctly more negative than the two-electron cathodic peaks E_1 of corresponding chloride systems but which are typical for organometallic complexes of bpy,¹² the complex (bpy)OsH(C₆Me₆) showed an irreversible second reduction at a very negative peak potential E_{11} (Scheme 5, Table 1).

EPR Spectroscopy of (bpy)OsH(C₆Me₆). The stability and reversible one-electron reduction of the osmium(II) hydride complexes allowed an *intra muros* generation of paramagnetic neutral species such as (bpy)OsH(C₆Me₆) for EPR investigation.

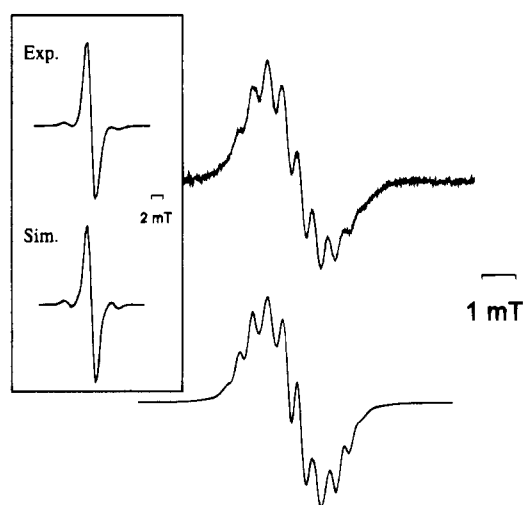


Figure 2. (Top) Experimental EPR spectrum (main signal) of electrochemically generated (bpy)OsH(C₆Me₆) in CH₃CN containing 0.1 M Bu₄NPF₆. (Bottom) Computer-simulated spectrum with $a(^{14}\text{N}) = 0.51$ mT (2N) and $a(^1\text{H}) = 0.35$ mT (5H) and a line width of 0.28 mT. (Inset) Experimental and simulated spectrum at lower resolution and higher S/N ratio, revealing the ¹⁸⁹Os isotope coupling of 2.63 mT (line width 0.36 mT).

The sufficiently well resolved spectrum (Figure 2; coupling constants $a \pm 0.1$ mT) does not possess a central line which suggests the coupling of the unpaired electron with an odd number of nuclei with non-integer nuclear spin. The obvious cause for such a situation is the coupling with the single hydride nucleus ($I = 1/2$; $a = 0.35$ mT). Incorporation of the three other expected²⁰ main coupling constants $a(^{14}\text{N}) = 0.51$ mT and $a(\text{H}^{5,5'}) = a(\text{H}^{4,4'}) = 0.35$ mT of what is apparently a bpy-based radical complex (bpy^{•-})Os^{II}H(C₆Me₆) produces a good agreement between experimental and simulated spectra. The coupling constants of the other nuclei in the aromatic ligands are not resolved due to the relatively high linewidth. However, a careful inspection of the expanded spectrum (Figure 2) reveals satellite lines from the interaction of the unpaired electron with the isotope ¹⁸⁹Os (16.1% natural abundance, $I = 3/2$).

Of the four metal isotope satellite lines, each with about 5% intensity of the main signal, the two outer ones are clearly visible albeit with slightly different peak heights due to selective line broadening.^{28a} With $a(^{189}\text{Os}) = 2.63$ mT the metal isotope

- (28) (a) Goodman, B. A.; Raynor, J. B. *Adv. Inorg. Chem. Radiochem.* **1970**, *13*, 135. (b) Morris, D. E.; Hanck, K. W.; DeArmond, M. K. *Inorg. Chem.* **1985**, *24*, 977.
 (29) (a) Memory, J. D.; Wilson, N. K. *NMR of Aromatic Compounds*; Wiley: New York, 1982. (b) Breitmaier, E.; Voelter, W. *Carbon-13 NMR Spectroscopy*; VCH: Weinheim, 1987; p 292.

Table 2. ¹H NMR Data^a for 2,2'-Bipyridine^b and Its Complexes

compound	solvent	δ (ppm) ^b					
		H ⁶	H ⁵	H ⁴	H ³	CH ₃ (Me/Pr)	other
bpy	CD ₃ CN	8.64	7.33	7.82	8.40		
bpy	C ₆ D ₆	8.52	6.67	7.20	8.73		
[(bpy)RhCl(C ₅ Me ₅)](PF ₆) ^c	CD ₃ CN	8.89	7.81	8.24	8.37	1.65	
[(bpy)Rh(C ₅ Me ₅)]	C ₆ D ₆	9.10	6.44	6.85	7.45	1.85	
[(bpy)IrCl(C ₅ Me ₅)](PF ₆)	CD ₃ CN	8.88	7.78	8.21	8.44	1.65	
[(bpy)Ir(C ₅ Me ₅)]	C ₆ D ₆	8.94	6.16	6.71	7.56	1.75	
[(bpy)IrH(C ₅ Me ₅)](BPh ₄) ^d	(CD ₃) ₂ CO	9.11	7.72	8.16	8.55	1.93	e
[(bpy)RuCl(C ₆ H ₆)](PF ₆)	CD ₃ CN	9.40	7.68	8.18	8.32		f
[(bpy)Ru(C ₆ H ₆)]	C ₆ D ₆	8.80	6.25	6.65	7.39		g
[(bpy)RuCl(<i>p</i> -Cym)](PF ₆)	CD ₃ CN	9.31	7.69	8.17	8.31	2.20/1.02	h, i
[(bpy)Ru(<i>p</i> -Cym)]	C ₆ D ₆	8.86	6.33	6.66	7.42	1.99/1.12	h, j
[(bpy)RuCl(C ₆ Me ₆)](PF ₆)	CD ₃ CN	8.85	7.72	8.13	8.29	2.05	
[(bpy)Ru(C ₆ Me ₆)]	C ₆ D ₆	8.73	6.56	6.73	7.56	1.96	
[(bpy)OsCl(<i>p</i> -Cym)](PF ₆)	CD ₃ CN	9.25	7.65	8.16	8.39	2.25/0.95	h, k
[(bpy)Os(<i>p</i> -Cym)]	C ₆ D ₆	8.63	5.98	6.43	7.45	1.94/1.02	h, l
[(bpy)OsH(<i>p</i> -Cym)](BPh ₄)	CD ₂ Cl ₂	8.89	7.26	7.82	7.97	2.34/1.13	h, m
[(bpy)OsCl(C ₆ Me ₆)](PF ₆)	CD ₃ CN	8.73	7.69	8.08	8.36	2.05	
[(bpy)Os(C ₆ Me ₆)]	C ₆ D ₆	8.45	6.29	6.57	7.66	1.87	
[(bpy)OsH(C ₆ Me ₆)](BPh ₄)	CD ₂ Cl ₂	8.65	7.30	7.73	7.94	2.20	n

^a Chemical shifts relative to internal SiMe₄. ^b Assignments according to established coupling constants for the 2-pyridyl group: ³J(H³-H⁴) ≈ 8 Hz; ³J(H⁴-H⁵) ≈ 7 Hz; ³J(H⁵-H⁶) ≈ 5 Hz. ^c Reference 13. ^d Reference 12a. ^e δ = -11.45 (M-H) and 6.78, 6.93, and 7.36 (BPh₄). ^f 6.02 (H_{arom.}). ^g 4.87 (H_{arom.}). ^h δ_{C-H}[Pr, H_{arom.}]. ⁱ [2.64, (5.91/5.71)]. ^j [2.48, (4.80/4.70)]. ^k [2.49, (6.13/5.87)]. ^l [2.25, (4.88/4.94)]. ^m [2.58, (5.35/5.53)]; δ = -5.93 (M-H) and 6.85, 7.00, and 7.33 (BPh₄). ⁿ δ = -7.40 (M-H) and 6.85, 7.00, and 7.33 (BPh₄).

coupling is fairly large, amounting to more than 2% of the corresponding isotropic hyperfine coupling constant $A_{\text{iso}} = 118.3$ mT for the metal;^{28a} similar values have recently been observed for ruthenium(II) complexes of strongly interacting anion radicals of azo ligands.^{30b}

The binding of an osmium(II) hydride fragment to bpy^{•-} is not just evident from the sizable metal and hydride hyperfine splitting due to sterically favored (Scheme 6) hyperconjugation $\sigma(\text{Os}-\text{H})/\pi^*(\text{bpy})$; the presence of a 5d metal with its very high spin-orbit coupling constant is also reflected by the distinctly lowered isotropic g factor of 1.981. Similar observations have been made previously for species such as $[\text{Os}(\text{bpy})_3]^+$ ($g = 1.989$) which exhibit unresolved EPR spectra,^{28b} with deviation to lower g factors relative to the values of the free electron ($g_e = 2.0023$) or of the free ligand $\text{bpy}^{\bullet-}$ ($g = 2.0030$) pointing to low-lying excited states²⁴ with non-zero angular orbital momentum.

¹H and ¹³C NMR Spectroscopy. As summarized in Table 2, the cationic d⁶ metal complexes generally display low-field shifts of the bpy proton resonances with regard to the free ligand in acetonitrile solution. The less pronounced low-field shifts of the hydrides relative to corresponding chloride complexes and the typical hydride resonances below -5 ppm are as expected. On the other hand, high-field shifts were observed for most bpy protons of the two-electron reduced neutral compounds in benzene solution (Figure 3).

The sequence for chemical shifts $\text{H}^{5,5'} \approx \text{H}^{4,4'} < \text{H}^{3,3'} < \text{H}^{6,6'}$ for complexes (bpy)M(C_nR_n) is in full agreement with the calculated and observed spin densities of the 2,2'-bipyridine anion radical;²⁰ the small low-field shift for H^{6,6'} even reflects the occurrence of a small negative spin density for those protons in the typical perturbation regime of $\text{bpy}^{\bullet-}$.²⁰ Of course, the protons H^{3,3'} are affected by the conformational change (trans → cis) on complexation and by the thus caused absence of C-H---N deshielding in the complexes. Even after considering the special effect²⁹ of the aromatic solvent C₆D₆ on the coordinatively unsaturated species (bpy)M(C_nR_n), the high-field

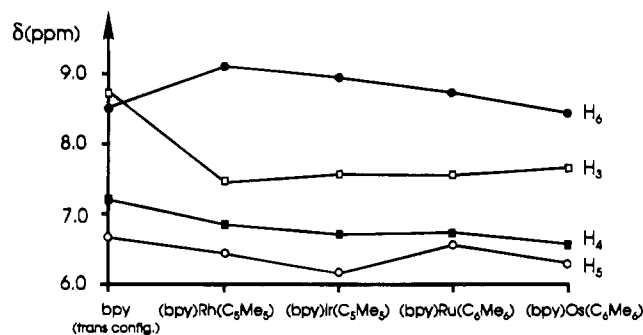


Figure 3. ¹H NMR chemical shifts of bpy and its complexes in C₆D₆.

shifts for the sterically unaffected protons H^{4,4'} and H^{5,5'} are obvious, reaching a minimum in case of the most sensitive²⁰ protons H^{5,5'} for the iridium and osmium systems and confirming a significant amount of negative charge transfer from the formally d⁸ configured metal center to the bpy ligand.

Similar effects were observed for the ¹³C NMR resonances, which are summarized in Table 3. Starting with the established assignments for free bpy,^{29b} the cationic chloride and hydride complexes exhibit slight low-field shifts of the corresponding resonances. On the other hand, the neutral complexes reveal that some resonances (C³, C⁴, C⁵) are strongly shifted to higher field, reflecting the metal-to-ligand charge transfer in the ground state of this form.

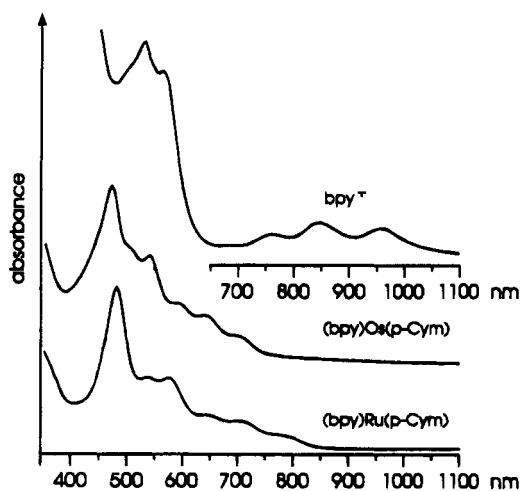
UV/Vis Spectroscopy. The cationic precursor complexes with d⁶ metal configuration exhibit two discernible but rather broad, featureless absorption bands in the visible and near UV regions (see Experimental Section) which can be attributed to ligand-to-metal charge transfer transitions (LMCT) from the halide and from the π -bonded C_nR_n donor ligands.¹³ In agreement with the electrochemical results which indicated a bpy-centered LUMO, the longer-wavelength absorptions of the isolated osmium(II) hydride complexes are attributed to (metal hydride)-to-bpy charge transfer transitions, involving a rather covalently bonded Os-H donor entity and the lowest π^* acceptor orbital of bpy. The transition energy of about 519 nm (2.39 eV) for the (hexamethylbenzene)osmium hydride complex correlates rather well with the difference $E_8 - E_1 = 2.41$ V between cathodic peak potentials (Table 1). More

(30) (a) Fees, J.; Kaim, W.; Moscherosch, M.; Matheis, W.; Klima, J.; Krejčík, M.; Zalis, S. *Inorg. Chem.* **1993**, *32*, 166. (b) Krejčík, M.; Zalis, S.; Klima, J.; Sykora, D.; Matheis, W.; Klein, A.; Kaim, W. *Inorg. Chem.* **1993**, *32*, 3362.

Table 3. ^{13}C NMR Data^a for 2,2'-Bipyridine and Its Complexes

compound	solvent	δ (ppm)					C_n/R_n
		C ²	C ³	C ⁴	C ⁵	C ⁶	
bpy	CD ₃ CN	156.8	121.4	137.2	124.0	149.4	
bpy ^b	C ₆ D ₆	157.5	121.8	137.3	124.4	150.1	
[(bpy)RhCl(C ₅ Me ₅)](PF ₆)	CD ₃ CN	154.9	124.3	140.9	128.9	152.5	97.9/8.7
[(bpy)Rh(C ₅ Me ₅)] ^c	C ₆ D ₆	136.5	120.7	122.8	116.0	149.8	88.9/9.8
[(bpy)Ir(C ₅ Me ₅)] ^c	C ₆ D ₆	141.0	117.6	123.4	115.3	147.9	83.5/9.7
[(bpy)IrH(C ₅ Me ₅)](BPh ₄) ^d	(CD ₃) ₂ CO	156.6	128.7	139.0	124.9	153.4	91.4/9.5
[(bpy)RuCl(C ₆ H ₆)](PF ₆)	CD ₃ CN	142.3	124.7	141.0	128.4	156.6	88.1/—
[(bpy)RuCl(<i>p</i> -Cym)](PF ₆)	CD ₃ CN	155.7	124.8	140.9	128.6	156.5	<i>e, f</i>
[(bpy)Ru(<i>p</i> -Cym)]	C ₆ D ₆	143.0	118.9	122.6	115.0	152.5	<i>e, g</i>
[(bpy)RuCl(C ₆ Me ₆)](PF ₆)	CD ₃ CN	146.3	124.4	140.5	128.6	154.5	96.9/15.8
[(bpy)Ru(C ₆ Me ₆)]	C ₆ D ₆	141.5	117.9	122.7	114.8	150.1	86.6/16.3
[(bpy)OsCl(<i>p</i> -Cym)](PF ₆)	CD ₃ CN	n.o.	124.9	140.9	129.4	156.4	<i>e, h</i>
[(bpy)Os(<i>p</i> -Cym)]	C ₆ D ₆	143.4	116.9	122.9	115.0	152.0	<i>e, i</i>
[(bpy)OsCl(C ₆ Me ₆)](PF ₆)	CD ₃ CN	n.o.	124.4	140.4	129.0	154.0	88.7/15.8
[(bpy)Os(C ₆ Me ₆)]	C ₆ D ₆	141.2	115.5	122.8	114.2	148.8	78.7/16.9
[(bpy)OsH(C ₆ Me ₆)](BPh ₄)	CD ₂ Cl ₂	n.o.	126.5	136.5	123.2	152.7	89.8/16.6 ^j

^a Chemical shifts relative to internal SiMe₄; tentative assignments of C³, C⁴, and C⁵ resonances; n.o. = not observed. ^b Assignments according to ref 29b. ^c Reassigned values from ref 13. ^d Reference 11d. ^e *p*-Cymene carbon centers (primed). ^f δ (ppm): C¹, 106.1; C^{2,6}, 87.5; C^{3,5}, 85.4; C⁴, 104.5; CH₃, 18.9; CH, 31.8; CH(CH₃)₂, 22.1. ^g δ (ppm): C¹, 98.7; C^{2,6}, 77.7; C^{3,5}, 75.1; C⁴, 87.1; CH₃, 19.0; CH, 32.2; CH(CH₃)₂, 24.1. ^h δ (ppm): C¹, 97.7; C^{2,6}, 79.0; C^{3,5}, 75.4; C⁴, 96.8; CH₃, 18.8; CH, 31.9; CH(CH₃)₂, 22.4. ⁱ δ (ppm): C¹, 90.8; C^{2,6}, 69.9; C^{3,5}, 67.2; C⁴, 79.4; CH₃, 20.1; CH, 33.1; CH(CH₃)₂, 24.2. ^j BPh₄⁻. δ (ppm): C¹, 163.8; C^{2,6}, 136.3; C^{3,5}, 123.1; C⁴, 122.1.

**Figure 4.** Absorption spectra of two complexes and of the bpy radical anion in THF solution (absorbance different for each spectrum).**Table 4.** Absorption Data^a for the Complexes and for the 2,2'-Bipyridine Radical Anion

compound	λ_{max} (nm)			$\Delta\nu$ (cm ⁻¹) ^b
	CT	IL ₂	IL ₁	
bpy ⁻		530, 564	760, 843, 956	1300, 1400
(bpy)Rh(C ₅ Me ₅) ^c	516	575 sh	682, 748, 830 sh	1290, 1320
(bpy)Ir(C ₅ Me ₅) ^c	489	534	620, 671, 733	1230, 1260
(bpy)Ru(C ₆ H ₆)	472	532 sh, 578	646 sh, 700 sh, 777 sh	1190, 1420
(bpy)Ru(<i>p</i> -Cym)	478	531, 572	645, 704, 780 sh	1300, 1380
(bpy)Ru(C ₆ Me ₆)	486	528 sh, 571	650, 710, 795 sh	1300, 1500
(bpy)Os(<i>p</i> -Cym)	471	504 sh, 538	591, 641, 700 sh	1320, 1320
(bpy)Os(C ₆ Me ₆)	474	528	599, 651, 713	1330, 1340

^a From measurements in THF solution. ^b Spacings between the three discernible components of transition IL₁. ^c From ref 12a.

detailed photochemical measurements should show whether the irradiation into this band is sufficient to cause photoinduced hydride transfer and H₂ production.^{11,30}

The two-electron reduced neutral compounds are distinguished by several intense absorption bands in the visible region. Figure 4 shows the spectra of two group 8 complexes together with the spectrum of bpy⁻, and Table 4 contains the relevant data for group 8 and group 9 complexes.

In each case the long-wavelength band system, IL₁, involves

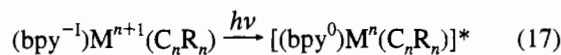
three discernible but relatively weak bands, the spacing of which (Table 4) suggests a vibrational splitting related to the aromatic diimine.^{15–19} The following two bands, IL₂, are somewhat more intense, the high-energy component sometimes being obscured by the main rather narrow band, CT, at about 490 nm. The next major features occur below 300 nm and shall not be discussed further.

The spectra in Figure 4 and the data show a striking correspondence between the spectrum of the bpy anion radical and the long-wavelength features of the complexes (bpy)M(C_nR_n). The lowest energy transition, i.e. the vibrationally structured three-component band system, has been attributed to a largely forbidden intraligand (IL₁) transition SOMO → LUMO or $\pi(7) \rightarrow \pi(8)$ in bpy⁻ and related systems.^{15–17} In the complexes, this band system experiences a high-energy shift (stabilization of the SOMO) and an intensity increase due to the lowered symmetry and spin-orbit coupling; both effects have been similarly observed for other free α -diimine anion radicals and their transition metal complexes.^{17b,31} For "normal" complexes of Rh(I) or Ir(I) with aromatic α -diimines, such fine structure has been observed only in the emission from the MLCT excited state (eq 2)^{18,19} which suggests a ground state electronic structure (**B**, Scheme 1) of compounds (bpy)M(C_nR_n) which corresponds to the formulation of MLCT excited states of "normal" complexes (eq 2).

In analogy to the situation in free bpy⁻, the second and somewhat stronger band system between 500 and 580 nm of complexes (bpy)M(C_nR_n) can be assigned to another well-known intra-ligand (IL₂) transition of the reduced heterocycle, $\pi(7) \rightarrow \pi(10)$.^{15–17} The most intense band around 490 nm can be viewed as a metal-to-ligand (eq 2) or ligand-to-metal (eq 17) charge transfer (CT) band involving the $\pi(7)$ orbital, presumably mixed with the equally allowed $\pi(6) \rightarrow \pi(7)$ transition which occurs around 400 nm in free bpy⁻.^{15–17,31} The mixed character of that transition is evident from the rather small bandwidth of about 2500 cm⁻¹ and the virtually absent solvatochromism as measured in detail for (bpy)Ir(C₅Me₅).^{12a} All long-wavelength band systems are hypsochromically shifted to about the same extent in the order of Rh < Ru \approx Ir < Os compounds

(increasing absorption energies).

Scheme 7



A comparison between optical and electrochemical data,³² i.e. between the longest wavelength transitions and corresponding peak potential differences $E_3 - E_4$ or $E_2 - E_5$ shows rather good agreements as exemplified by values $\lambda_{\text{max}} = 717 \text{ nm}$ ($E_{\text{max}} = 1.73 \text{ eV}$) and $E_3 - E_4 = 1.74 \text{ V}$ for (bpy)Os(C₆Me₆).

Comparative Discussion and Conclusions

It is clear from the data in Tables 1–4 that, within a certain type of metal complexes—[(bpy)MX(C₆R₆)]⁺ (X = Cl, H) or (bpy)M(C₆R₆)—the alkyl substitution at the arene ligands influences the physical properties, the donor strength increasing along the series C₆H₆, *p*-MeC₆H₄iPr, and C₆Me₆. For comparison with the rhodium and iridium cyclopentadienide systems we shall mainly use the hexamethylbenzene derivatives of the group 8 metal complexes in the following.

Regarding electrochemistry, Table 1 shows that the peak potential E_1 for cathodic reduction is most negative for the 5d systems and least negative for the rhodium complex. This value and its dependence on substituents are important for the critical first step (eq 4) of reductive activation of electrophiles such as H⁺. The peak potential difference $E_1 - E_2$ for that first irreversible step is largest for the iridium system, presumably due to the strong bond between chloride and the trivalent 5d metal. Re-coordination to the electrogenerated dication [(bpy)M(C_nR_n)]²⁺ is slowed down considerably in substituted arene-containing group 8 metal complexes because of steric constraints; the corresponding re-reduction (E_3) is not observable for the group 9 systems unless the α -diimine ligand provides considerable steric hindrance.¹⁴

A similar stabilizing effect is observed for the oxidation of the d⁶ metal-containing cations which is reversible only for the hexamethylbenzene complexes; the peak potential E_7 decreases in the order Rh > Ru > Os > Ir compounds.

One of the most remarkable properties of the neutral complexes (bpy)M(C_nR_n) is that their one-electron bpy-centered reduction occurs at more negative potentials than that of free bpy. The charge-withdrawing effect of the metal which otherwise facilitates the reduction of coordinated bpy¹² even

when supposedly electron-rich organometal fragments such as Zn(*t*-Bu)₂ or Mo(CO)₂(PR₃)₂ are coordinated is obviously more than compensated by the unique π back-donating capability of the M(C_nR_n) fragments. The strongest such effect, $E_6 - E_4$, has now been established for (bpy)Os(C₆Me₆) (Table 1). The smallest but still remarkable effect occurs in the rhodium complex of bpy; with other α -diimine ligands the rhodium systems were shown to exhibit a characteristic dependence on the acceptor capability of those ligands.^{13,14} These results can only be understood when a considerable contribution from resonance form (**B**, Scheme 1) is taken into account.

In summary, all available data from electrochemistry, spectroscopy (NMR, UV/vis), reactivity^{12a} and structure^{11c} for the complexes (α -diimine)M(C_nR_n) point to a sizable contribution from resonance structure **B**, i.e. to an extraordinary amount of charge transfer from the metal to the α -diimine acceptor ligand in the ground state. The resulting charge distribution is normally observed for MLCT excited states of α -diimine complexes (eq 2),^{18,19,32,33} with less electron rich metal complex fragments such “ground state modeling of excited states” occurs only when extremely strong acceptor ligands such as TCNE are being used.^{23b} While the charge distribution is thus established, the exact spin state could not be determined here by susceptibility measurements due to the high sensitivity of the intermediates. It can be speculated, however, that strong antiferromagnetic spin coupling²³ between the anion radical ligand and the low-spin d⁷ metal center renders the complexes without obvious paramagnetism.

For the catalytic hydride transfer mechanism which involves reactions 4, 5, 12, 15, and 7 (Schemes 4 and 5),⁸ the electrochemical difference between halide and hydride complexes is crucial. Whereas the halide complexes undergo an at least partially metal-centered two-electron reduction with concomitant loss of the halide, the hydride complexes display a reversible bpy-centered one-electron reduction at more negative potentials. While the 5d systems form stable hydrides which require additional activation, e.g. in the form of light, for hydride transfer, the 4d systems react to more labile and thus catalytically more suitable hydride intermediates. However, the arene rings of Ru(C₆R₆) complexes are more labile than the cyclopentadienide ligands of Rh(C₅R₅) with their additional electrostatic bonding, leaving the rhodium complexes as the most stable and efficient hydride transfer catalysts^{8–10} within the series described here.

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