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Resolving the Two-Electron Process for the Couple $[(C_5Me_5)M(N^\wedge N)Cl]^+/[(C_5Me_5)M(N^\wedge N)]$ (M = Rh, Ir) into Two One-Electron Steps Using the 2,2′-Azobis(pyridine) N^N Ligand, Fast Scan Cyclovoltammetry, and Spectroelectrochemistry: Detection of Radicals instead of M^{II} Intermediates

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The complex cations $[(C_5Me_5)M(abpy)Cl]^+$ (M = Rh, Ir; abpy = 2,2′-azobis(pyridine)) are reduced to the coordinatively unsaturated compounds $[(C_5Me_5)M(abpy)]$ via the EPR and UV/vis spectroelectrochemically detectable radical intermediates $[(C_5Me_5)M^{III}(abpy^{-I})Cl]^{\bullet}$. Fast-scan cyclic voltammetry allowed us to establish the electrochemical potentials. This stepwise mechanism differs from the two-electron processes observed for the analogous systems $[(C_5Me_5)M(N^\wedge N)Cl]^+/[(C_5Me_5)M(N^\wedge N)]$ with N^N = 2,2′-bipyridines, bidiazines, 1,4-diaza-1,3-butadienes. In contrast to cobalt systems such as $[(C_5Me_5)Co(bpy)Cl]^+$ the one-electron reduction does not involve the metal. The role of the abpy ligand as an intermediate one-electron storage component for a metal-centered two-electron process is discussed. Further reduction of $[(C_5Me_5)M(abpy)]$ to $[(C_5Me_5)M^{II}(abpy^{-II})]^-$ at very negative potentials illustrates the extremely strong π back-donation from the 14-valence-electron fragments $(C_5Me_5)M$ (M = Rh, Ir).

Introduction

Hydride transfer catalysis[1] is important for the generation of fuels (e.g. H_2 from H^+)[2] and for the regeneration of NADH from NAD^+ during biotechnological processes.[3] One such well-researched catalyst system has $[(C_5Me_5)Rh(bpy)Cl]^+$ as precursor, which is reductively converted in a two-electron step to the highly reactive $[(C_5Me_5)Rh(bpy)]$.[2,4] That latter compound can react with H^+ to form the active hydride intermediate $[(C_5Me_5)Rh(bpy)H]^+$, which is the actual hydride-transferring species within the catalytic cycle of Scheme 1.[1,2,4]

The intermediates of Scheme 1 can be stabilized through replacement of Rh by Ir (→ stable hydride form)[5] and through changing the chelate ligand to sterically shielding 1,4-diaza-1,3-butadienes (→ stable neutral form).[6] In all instances (N^N = 2,2′-bipyridines,[2−5] bidiazines,[4c] 1,4-diaza-1,3-butadienes[6,7]), however, the activation step is an ECE or EEC process (eq 1), as confirmed electrochemically, for which the second

$$[(C_5Me_5)M(N^\wedge N)Cl]^+ + 2e^- \rightleftharpoons [(C_5Me_5)M(N^\wedge N)] + Cl^- \quad (1)$$

$$[(C_5Me_5)Co^{III}(bpy)Cl]^+ + e^- \rightleftharpoons [(C_5Me_5)Co^{II}(bpy)]^+ + Cl^- \quad (2)$$

$$[(C_5Me_5)Co^{II}(bpy)]^+ + e^- \rightleftharpoons [(C_5Me_5)Co^{I}(bpy)] \quad (3)$$

reduction occurs at a more positive potential than the first one, resulting in an overall 2e transfer. Only with cobalt instead of rhodium or iridium was a one-electron, i.e., a cobalt(II), intermediate established within an EC + E sequence (eqs 2 and 3).[8]

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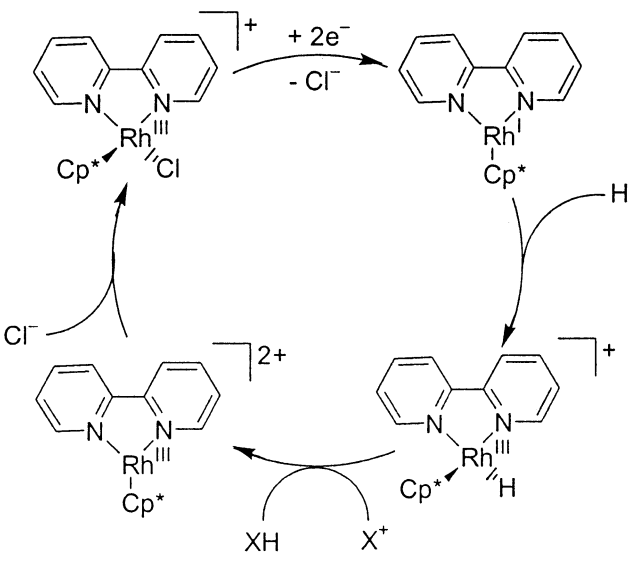
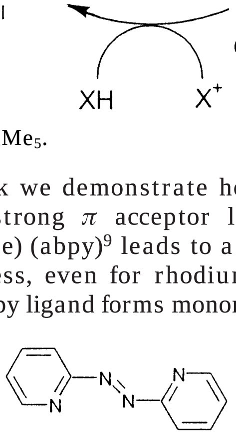
10.1021/om020860j CCC: $25.00

Scheme 1 [a]

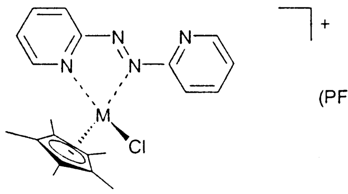


[a] $Cp^* = \eta^5\text{-}C_5Me_5$.

In this work we demonstrate how the choice of the particularly strong π acceptor ligand N^N = 2,2′-azobis(pyridine) (abpy)[9] leads to a splitting of the two-electron process, even for rhodium and iridium complexes. The abpy ligand forms mononuclear and dinuclear metal complexes with unusual properties, including very long wavelength charge-transfer bands, efficient metal−metal interaction, and stable radical states.[9] The well-known reluctance of rhodium or iridium to form a divalent state is thus circumvented by providing a very strong π acceptor ligand for one-electron storage in the corresponding intermediate $[(C_5Me_5)M^{III}(abpy^{-I})Cl]^{\bullet}$ containing the abpy radical anion ($abpy^{-I}$).



abpy



M = Rh or Ir

Experimental Section

Instrumentation. EPR spectra were recorded in the X-band on a Bruker System ESP 300 equipped with a Bruker ER035M gauss meter and a HP 5350B microwave counter. ^1H NMR spectra were taken on a Bruker AC 250 spectrometer. UV/vis/near-IR absorption spectra were recorded on Shimadzu UV160 and Bruins Instruments Omega 10 spectrophotometers. Cyclic voltammetry was carried out in acetonitrile/0.1 M Bu_4NPF_6 using a three-electrode configuration (glassy-carbon working electrode, Pt counter electrode, Ag/AgCl reference) and a PAR 273 potentiostat and function generator. The ferrocene/ferrocenium couple ($Fc^{+/0}$) served as internal reference. Fast-scan cyclic voltammetry was performed using a custom-built potentiostat modeled after instruments from the Ecole Normale Superieure (Paris, France; Prof. C. Amatore). Gold or platinum ultramicroelectrodes (25, 50, or 125 μm) were used in this instance; the data were collected with a Nicolet 410 oscilloscope. Spectroelectrochemical measurements were performed using an optically transparent thin-layer electrolysis (OTTLE) cell[10] for UV/vis spectra and a two-electrode capillary for EPR studies.[11]

$[(C_5Me_5)Rh(abpy)Cl](Cl)$. A suspension of 74 mg (0.120 mmol) of $[(C_5Me_5)Rh(\mu\text{-}Cl)Cl]_2$[12] in 40 mL of acetone was stirred for 3 days with 44 mg (0.239 mmol) of abpy.[13] The orange product was filtered off, washed with diethyl ether, and dried under vacuum to yield 80 mg (70%) of product. Anal. Calcd for $C_{20}H_{23}Cl_2N_4Rh$ (493.25): C, 48.70; H, 4.70; N, 11.36. Found: C, 48.45; H, 4.78; N, 11.12%. ^1H NMR (CD_3CN): δ 1.65 (s, 15H; Cp*), 7.79 (ddd, 1H; $H^{5'}$), 8.05 (Dddd, 1H; H^5), 8.12 (dt, 1H; $H^{3'}$), 8.717 (td, 1H; $H^{4'}$), 8.49 (td, 1H; H^4), 8.80 (dd, 1H; H^3), 8.88 (ddd, 1H; $H^{6'}$), 8.99 (dd, 1H; H^6); $^3J(H^3,H^4) = 7.8$ Hz, $^3J(H^{3'},H^{4'}) = 8.4$, $^3J(H^4,H^5) = 7.8$, $^3J(H^{4'},H^{5'}) = 7.1$, $^3J(H^5,H^6) = 5.4$, $^3J(H^{5'},H^{6'}) = 4.7$ Hz.

$[(C_5Me_5)Ir(abpy)Cl](PF_6)$. A suspension of 156 mg (0.196 mmol) of $[(C_5Me_5)Ir(\mu\text{-}Cl)Cl]_2$[14] in 40 mL of CH_3OH was reacted with 90 mg (0.489 mmol) of abpy for 3 h. The greenish solution was reduced to about 10 mL and treated with ca. 3 equiv of Bu_4NPF_6 in methanol. The olive green precipitate was filtered, washed with methanol and diethyl ether, and dried under vacuum. Yield: 255 mg (95%). Anal. Calcd for $C_{20}H_{23}ClF_6IrN_4P$ (692.08): C, 34.71; H, 3.35; N, 8.10. Found: C, 34.63; H, 3.42; N, 7.99. ^1H NMR (CD_3CN): δ 1.72 (s, 15H, CH_3Cp^*), 7.76 (ddd, 1H, $H^{5'}$(R)), 8.05 (m, 1H, H^5(R)), 8.09 (t, 1H, $H^{3'}$(R)), 8.17 (dt, 1H, $H^{4'}$(R)), 8.41 (dt, 1H, H^4(R)), 8.83 (ddd, 1H, $H^{6'}$(R)), 8.89 (ddd, 1H, H^6(R)), 8.96 (ddd, 1H, $H^{3'}$(R)) ppm; $^3J(H^3,H^4) = 8$, $^3J(H^4,H^5) = 7.7$, $^3J(H^5,H^6) = 5.6$, $^3J(H^{3'},H^{4'}) = 8.1$, $^3J(H^{5'},H^{6'}) = 5$ Hz.

$[(C_5Me_5)Rh(abpy)]$. A suspension of 30 mg (0.061 mmol) of $[(C_5Me_5)Rh(abpy)Cl](Cl)$ in 20 mL of THF was reacted under argon with a potassium mirror generated from 50 mg (1.3 mmol) of potassium. After 5 min the solution was filtered and reduced to dryness. Extraction with C_6H_6 and removal of the solvent gave 17 mg (65%) of a very air-sensitive dark blue material (no analysis). ^1H NMR ($[D_6]$acetone): δ 1.91 (s, 15H; Cp*), 6.40 (ddd, 1H; H^5), 7.00 (ddd, 1H; H^4), 7.14 (ddd, 1H; $H^{5'}$), 7.58 (d, 1H; H^3), 7.67 (ddd, 1H; $H^{4'}$), 7.81 (d, 1H; $H^{3'}$), 8.54 (ddd, 1H; H^6), 8.73 (d, 1H; H^6); $^3J(H^6,H^5) = 6.6$, $^3J(H^{6'},H^{5'}) = 4.8$, $^3J(H^5,H^4) = 5.5$, $^3J(H^{5'},H^{4'}) = 7.0$, $^3J(H^4,H^3) = 8.8$, $^3J(H^{4'},H^{3'}) = 8.3$ Hz.

$[(C_5Me_5)Ir(abpy)]$. A suspension of 33.2 mg (0.048 mmol) $[(C_5Me_5)Ir(abpy)Cl](PF_6)$ in 10 mL CH_3CH_2OH and 2.5 mL H_2O was treated at −10 °C with 18.5 mg (0.072 mmol) Bu_4NBH_4. The orange solution was reduced in volume until an orange-red precipitate formed which was then filtered, washed with water and dried under vacum. Extraction with toluene/*n*-hexane and removal of the solvent mixture gave a very air-sensitive red material (no analysis). ^1H NMR (C_6D_6): δ 1.65 (s, 15H; $CH_3(Cp^*)$), 5.99 (dt, $^3J = 6.6$ Hz, H^5(R)), 6.62 (ddd, 1H, H^4), 6.7 (ddd,1H, $H^{5'}$(R)), 7.25 (ddd, 1H, $H^{4'}$(R)), 7.99 (td, 1H, H^3), 8.32 (ddd, 1H, $H^{3'}$), 8.52 (d, 1H, H6), 8.54 (q, 1H, $H^{6'}$) ppm; $^3J(H^3,H^4) = 7.8$ Hz, $^3J(H^4,H^5) = 6.6$ Hz, $^3J(H^5,H^6) = 4$ Hz, $^3J(H^{3'},H^{4'}) = 7.3$ Hz, $^3J(H^{4'},H^{5'}) = 5$ Hz, $^3J(H^{5'},H^{6'}) = 2.1$ Hz.

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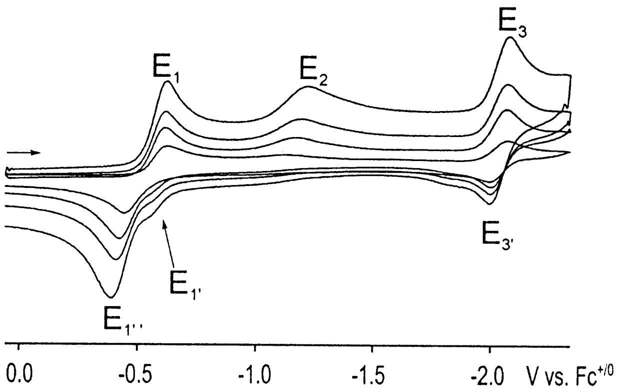

Figure 1. Cyclic voltammograms of $[(C_5Me_5)Rh(abpy)Cl](Cl)$ in $CH_3CN/0.1$ M Bu_4NPF_6 at 1, 3, 5, and 10 V/s scan rate (increasing current).

Results and Discussion

Synthesis and Identification. The precursor complexes $[(C_5Me_5)M(abpy)Cl](X)$ (M = Rh, X = Cl; M = Ir, X = PF_6) were obtained from $[(C_5Me_5)M(\mu\text{-}Cl)Cl]_2$[12,14] by following established procedures.[4−6] The activated neutral compounds $[(C_5Me_5)M(abpy)]$ could be obtained as very air-sensitive substances by reduction with potassium or with certain hydrides.[5c,6,15] Their identity was established by ^{1}H NMR via the significant[4c,5c] high-field shifts of H^4 and H^5 and confirmed by UV/vis/near-IR spectroscopy in connection with the spectroelectrochemical studies (see below). Remarkably, the iridium complex reacted to give diamagnetic $(C_5Me_5)Ir(abpy)$ with $(Bu_4N)(BH_4)$ in aqueous ethanol but gave mainly EPR-active $[(C_5Me_5)Ir(abpy)Cl]^\bullet$ on reaction with $Na[BH_3(CN)]$ (see below).

Electrochemistry. Irreversible oxidation was observed for the iridium complex, in agreement with previous reports.[5,6,15] The high value of $E_{p,a} = +1.48$ V vs $Fc^{+/0}$ reflects the lower basicity of abpy[9] in comparison to, for example, bpy ($E_{p,a} = +0.7$ V for $[(C_5Me_5)Ir(bpy)Cl]^{2+/+}$);[5c] high values similar to those for the abpy complex were obtained for analogous compounds with 1,4-diaza-1,3-butadienes.[6,15] The complex reduction behavior of the compounds was investigated using variable-scan-rate cyclic voltammetry.

At slow scan rates <500 mV/s the cyclic voltammograms appeared like those of other systems $[(C_5Me_5)M(N{\wedge}N)Cl]^+$, showing an irreversible two-electron conversion to $[(C_5Me_5)M(N^\wedge N)]$ with widely separated peak potentials E_1 and $E_{1''}$.[4,5] In agreeement with previous observations[4c,5c,8] the neutral compounds are reversibly reduced to $[(C_5Me_5)M(N^\wedge N)]^-$ at $E_3/E_{3'}$. At scan rates greater than 1 V/s the cyclic voltammograms exhibit additional features: a second cathodic peak emerges at E_2 and the anodic counter peak of the first wave at E_1 appears as a shoulder at the potential $E_{1'}$ (Figure 1).

When cyclic voltammetry is performed in an excess of chloride (Bu_4NCl), the peak signal E_2 appears at even lower scan rates and the current intensity of E_1 is decreased.

The results for both the rhodium and iridium complexes are very similar. The latter system was studied in further detail by rapid-scan voltammetry using ultramicroelectrodes (Figure 2). These studies showed both the anodic counter peak $E_{1'}$ to E_1 and the cathodic counter peak $E_{1'''}$ to $E_{1''}$.

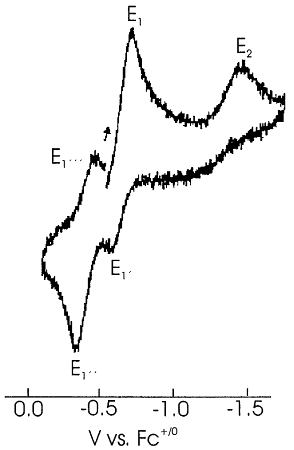

Figure 2. Cyclic voltammogram of $[(C_5Me_5)Ir(abpy)Cl](PF_6)$ in $CH_3CN/0.1$ M Bu_4NPF_6 at 10 V/s scan rate (125 μm Pt electrode).

Obviously, the chloride release after the first electron uptake is rather slow, allowing to detect intermediates by rapid scan voltammetry and spectroscopy (cf. below). After reduction by a second electron at E_2 there is rapid loss of Cl^- and an anodic counter peak could not be detected even at scan rates up to 5000 V/s. The presence of excess Cl^- stabilized the intermediate $[(C_5Me_5)M(abpy)Cl]^\bullet$, which was later used in the spectroelectrochemical investigation (see below).

The electrochemical potentials are summarized in Table 1; eqs 4−9 define the different processes.

$$[(C_5Me_5)M^{III}(abpy)Cl]^+ + e^- \underset{E_{1'}}{\overset{E_1}{\rightleftharpoons}} [(C_5Me_5)M^{III}(abpy^{-I})Cl]^\bullet \quad (4)$$

high v limit:

$$[(C_5Me_5)M^{III}(abpy^{-I})Cl]^\bullet + e^- \xrightarrow{E_2} [(C_5Me_5)M^n(abpy^{1-n})] + Cl^- \quad (5)$$

low v limit:

$$[(C_5Me_5)M^{III}(abpy^{-I})Cl]^\bullet \xrightarrow{L} [(C_5Me_5)M^{III}(abpy^{-I})L]^+ + Cl^- \quad (6)$$

$$[(C_5Me_5)M^{III}(abpy^{-I})L]^+ + e^- \xrightarrow{E_1} [(C_5Me_5)M^n(abpy^{I-n})] + L \quad (7)$$

L = solvent

$$[(C_5Me_5)M^n(abpy^{I-n})] - 2e^- \underset{E_{1'''}}{\overset{E_{1''}}{\rightleftharpoons}} [(C_5Me_5)M^{III}(abpy)]^{2+} \quad (8)$$

$$[(C_5Me_5)M^n(abpy^{I-n})] + e^- \underset{E_{3'}}{\rightleftharpoons} [(C_5Me_5)M^n(abpy^{-n})]^- \quad (9)$$

While the E_1 potentials are slightly less negative for the iridium analogue in comparison to the rhodium system, the E_3 potentials are much more negative in

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Table 1. Redox Potentials According to Eqs 4−8 from Cyclic Voltammetry

M	E_1	$E_{1'}$	E_1(1/2)	$E_{1''}$	$E_{1'''}$	E_2	E_3	$E_{3'}$	E_3(1/2)
Rh	−0.59	−0.53	−0.56	−0.49	n.o.	−1.08	−2.07	−2.00	−2.04
Ir	−0.55	−0.46	−0.51	−0.35	−0.42[b]	−1.11	−2.41	−2.35	−2.38

[a] Potentials in V vs $Fc^{+/0}$, standard scan rate 1 V/s. [b] Value measured at 10 V/s scan rate.

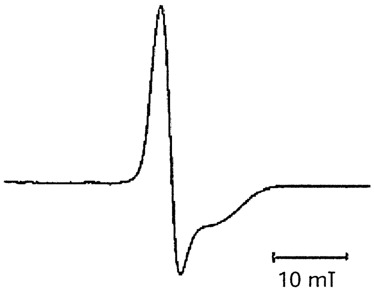

Figure 3. EPR spectrum of $[(C_5Me_5)Ir(abpy)Cl]^\bullet$ from brief in situ reduction (1 e) of $[(C_5Me_5)Ir(abpy)Cl](PF_6)$ in CH_3CN/0.1 M Et_4NPF_6 at 110 K.

the case of M = Ir. This observation reflects the stronger π donating capacity of (C_5Me_5)Ir relative to (C_5Me_5)Rh. Remarkably, both E_3(1/2) values lie much *more negative* (by more than 0.6 V!) than the reduction potential of free abpy at −1.37 V,[9] indicating that the π back-donation from (C_5Me_5)M far overcompensates the metal−ligand σ polarizing effect. With other π-electron-donating metal complex fragments such as $Re(CO)_3Cl$, $Mo(CO)_4$, and $[Ru(bpy)_2]^{2+}$ the reduction potentials are shifted by about 0.5 V to *less negative* values.[16]

Spectroelectrochemistry. EPR. Identification of the electrochemical intermediates, including their proper oxidation state assignment, has been achieved by using EPR spectroscopy for paramagnetic states and UV/vis/near-IR spectroscopy. In situ electrolysis provided the primary reduction products $[(C_5Me_5)M^{III}(abpy^{-I})Cl]^\bullet$ for EPR analysis. The rhodium complex showed only an unresolved line of 2.4 mT width at g_{iso} = 1.998, at both 298 and 4 K. Similar values were reported for ruthenium(II) complexes of $abpy^{\bullet -}$.[11] The iridium analogue (which could also be obtained via single-electron transfer[15,17] in the reaction with $Na[BH_3(CN)]$) showed g_{iso} = 1.983 at 298 K. In frozen solution at 110 K the signal split into $g_{1,2}$ = 1.995 and g_3 = 1.966 (Figure 3). This splitting and the sizable deviation from the free-electron value of g_e = 2.0023 are attributable to the large spin−orbit coupling contributions from the 5d element iridium;[18] however, an increased spin transfer from $abpy^{\bullet -}$ to Ir relative to Rh cannot be ruled out. The lowered g values in comparison to g_e point to a situation with close-lying unoccupied MOs, possibly the empty metal d orbitals which get involved in the chloride ligand labilization.

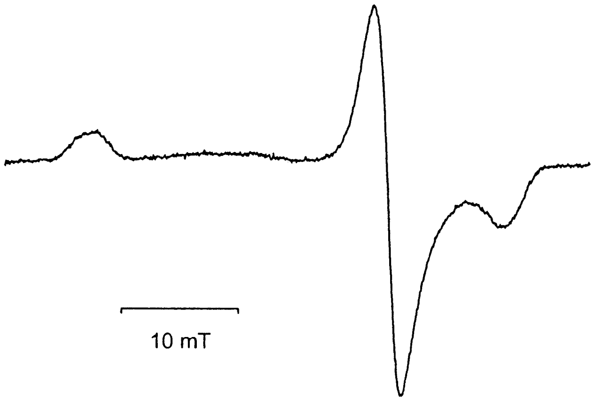

Figure 4. EPR spectrum of $[(C_5Me_5)Rh(abpy)]^{\bullet -}$ obtained after long-time in situ reduction (3 e) of $[(C_5Me_5)Rh(abpy)Cl](Cl)$ in CH_3CN/0.1 M Bu_4NPF_6 at 4 K.

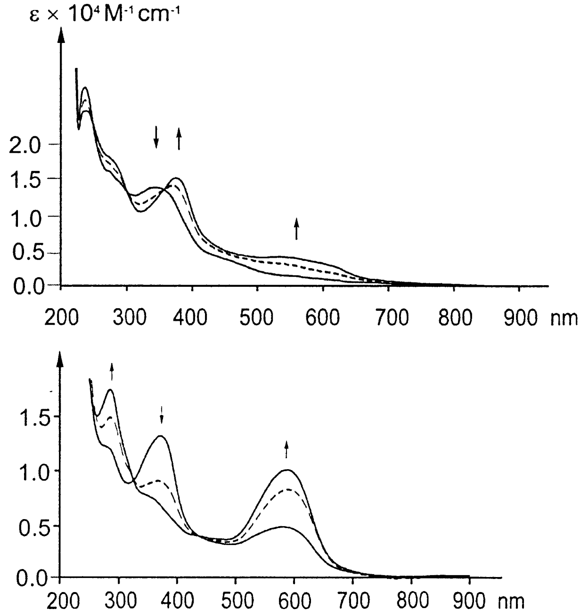

Figure 5. UV−vis spectral changes on reduction of $[(C_5Me_5)Rh(abpy)Cl](Cl)$ in CH_3CN/0.1 M Bu_4NCl at −0.7 V vs $Fc^{+/0}$: during the first 1 min (top) and after 1 min until formation of $(C_5Me_5)Rh(abpy)$ (bottom).

For the rhodium system it was possible to obtain an EPR spectrum of the three electron-reduced species $[(C_5Me_5)Rh^n(abpy^{-n})]^-$ (Figure 4) after continued electrolysis beyond the EPR-silent neutral state. Both the isotropic g value of 2.042 and the components at g_1 = 2.161, g_2 = 2.002, and g_3 = 1.945 indicate a paramagnetic species with largely metal-centered spin. For the oxidation state distribution a rhodium(0) formulation with neutral abpy (n = 0) or a rhodium(II) alternative (n = 2) with the organohydrazido(2−) ligand $abpy^{2-}$ can be discussed. In light of arguments from electrochemistry (very negative E_3(1/2)) and spectroscopy (see below) as well as structural and theoretical results for corresponding diazabutadiene complexes[6,19] we favor the Rh^{II} alternative. The iridium analogue could not be observed by EPR either because of rapid relaxation or due to diminished stability at the even more negative potential.

UV−Vis. The spectroelectrochemical studies with an OTTLE cell[10] had to be performed in the presence of excess chloride in order to counteract the Cl^- dissocia-

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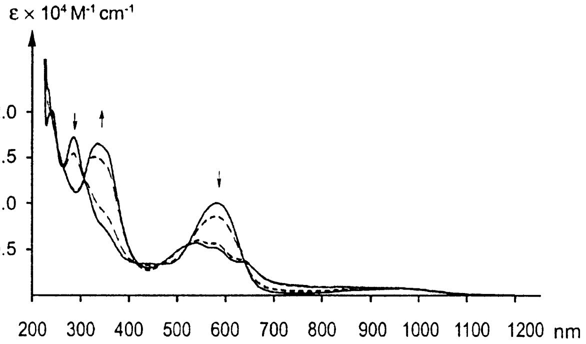

Figure 6. UV−vis spectral changes on reduction of [(C_5Me_5)Rh(abpy)] in CH_3CN/0.1 M Bu_4NPF_6.

Table 2. UV−vis Absorption Maxima λ_{max} (ϵ)[a] of Complexes in Acetonitrile[b]

complex	M	λ_{max} ($10^{-3}\epsilon$)
[(C_5Me_5)M(abpy)Cl]$^+$	Rh	450 sh, 345 (13.0)
	Ir	617 (0.5), 462 (3.6), 344 (10.6)
[(C_5Me_5)M(abpy)Cl]$^\bullet$	Rh	550 sh, 380 (14.0)
	Ir	500 sh, 385
[(C_5Me_5)M(abpy)]	Rh	585 (10.0),[c] 284 (17.0)
	Ir	488 (17.0), 355 sh, 282 (18.9)
[(C_5Me_5)M(abpy)]$^-$	Rh	636 sh, 579 sh, 540 (6.0), 335 (16.0)
	Ir	630 sh, 567 (7.1), 535 sh, 476 sh, 345 (15.3)

[a] λ_{max} in nm, molar extinction coefficients ϵ in M^{-1} cm^{-1}. [b] From spectroelectrochemistry in CH_3CN/0.1 M Bu_4NPF_6, Et_4NPF_6, or Bu_4NCl (cf. text). [c] λ_{max} = 600 nm in THF solution of synthesized complex.

tion (eqs 5 and 6). The spectral changes for eq 4 (M = Rh) are shown in Figure 5 (top), which also depicts the formation of [(C_5Me_5)Rh(abpy)] (eq 5). Further reduction to the rhodium(II)-containing anion is illustrated in Figure 6; Table 2 summarizes the absorption data.

The absorption data from spectroelectrochemistry support the oxidation state assignments in eqs 4−9. The cationic precursors have long-wavelength bands attributable to σ(M−Cl)-to-π^*(abpy) transitions.[19] The weak band at 617 nm for the iridium complex may be assigned to a partially allowed triplet transition, enhanced in intensity through spin−orbit coupling. Bands at about 550 and 400 nm are typical for abpy$^{\bullet-}$ and its complexes.[9,16] The neutral compounds [(C_5Me_5)M^n(N^N^{1-n})] are distinguished by intense bands at long wavelengths, assigned to allowed CT transitions between d_π orbitals of the metal and π^*(N^N).[4c,5c,8,19] Depending on the oxidation state formulation, these are MLCT (n = 1) or LMCT processes (n = 3). In fact, experiments and calculations for different ligands N^N suggest strong mixing between these π orbitals with highly variable contributions from either the metal or the N^N ligand side.[19] The spectroelectrochemical results were complemented by measurements on chemically prepared compounds [(C_5Me_5)M(N^N)]. On further reduction the long-wavelength band is replaced by broader, less intense, and partially structured features, some extending into the near-infrared region (Figure 6).

Conclusions

Using the special[9] N^N chelate ligand abpy, we could demonstrate for the first time for mononuclear complexes[20] how such an electron reservoir ligand can store a first electron before the combination with the second electron leads to chemical reactivity: here the reversible dissociation of Cl^- in a catalytically relevant activation step. This study is thus complementary to the many investigations on the separation of *reversible* 2e waves into one-electron processes.[21] The facile radical anion formation of the abpy ligand due its low-lying π^* orbital helps to circumvent unfavorable Rh^{II} or Ir^{II} intermediates. However, a Rh^{II} species has been identified by EPR spectroscopy for [(C_5Me_5)Rh(abpy)]$^{\bullet-}$. As for the iridium analogue, this anion is formed at a far more negative potential than the free abpy ligand, thereby illustrating the extraordinary capacity of the fragments (C_5Me_5)M, especially of (C_5Me_5)Ir with its established unusual chemistry,[22] for π back-donation.

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