

Electronic structure of catalytic intermediates for production of H₂: (C₅Me₅)Ir(bpy) and its conjugated acid

Monika Ladwig and Wolfgang Kaim

*Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55,
 W-7000 Stuttgart 80 (Germany)*

(Received March 11, 1992)

Abstract

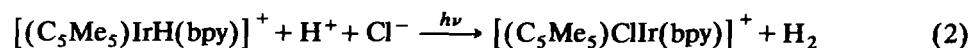
Chemical and electrochemical two-electron reduction of the Ir^{III} complex [(C₅Me₅)ClIr(bpy)](Cl), bpy = 2,2'-bipyridine, yields highly reactive (C₅Me₅)Ir(bpy), the conjugated acid of which was postulated as an intermediate in the homogeneous photo-catalysis of the water gas shift reaction. Cyclic voltammetric, UV/Vis-, ¹H- and ¹³C-NMR-spectroscopic measurements in aprotic and protic solvents have revealed the electronic structures of the neutral "Ir^I" complex and of [(C₅Me₅)IrH(bpy)]⁺. In the very electron-rich neutral complex there is even more π back donation to bpy than in the analogous compound (C₅Me₅)Rh(bpy), as is evident from the very negative reduction potential, the high field NMR shifts for the bpy ligand, and from the unusually structured absorption spectrum in the visible. As a consequence, the photo- and electro-chemical behaviour of [(C₅Me₅)IrH(bpy)]⁺ and [(C₅Me₅)Ir(bpy)] is best described by assigning a (-I) oxidation state to the electron-buffering 2,2'-bipyridine ligand.

Introduction

The photocatalysis of the water gas shift reaction (eq. 1), a H₂-producing two-electron redox process, by the homogeneous iridium-based system [(C₅Me₅)ClIr(bpy)]⁺, bpy = 2,2'-bipyridine, has been discussed in mechanistic terms in a recent communication by Ziessel [1].

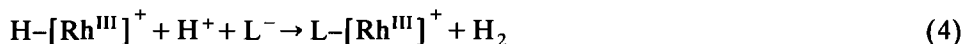


The postulated catalytic mechanism [1] involves the conjugated acid [(C₅Me₅)IrH(bpy)]⁺ [2] of the two-electron reduced species (C₅Me₅)Ir(bpy), which upon excitation with visible light ensures the completion of the catalytic cycle by reacting with a proton to generate dihydrogen (eq. 2).



Correspondence to: Professor W. Kaim.

A similar catalytic sequence involving the formation of a monohydride (eq. 3), and protonation of the latter to yield dihydrogen in exchange for an innocent ligand L (eq. 4) was reported for the related rhodium system [3].



L^- e.g. Cl^- ; $[\text{Rh}] = (\text{C}_5\text{Me}_5)\text{Rh}(\text{bpy})$

Here we describe the chemical and electrochemical formation of the hydride complex (eq. 2) and of its conjugate base $(\text{C}_5\text{Me}_5)\text{Ir}(\text{bpy})$, their spectral properties (^1H -, ^{13}C -NMR, UV/Vis), and attempt to understand the function of the π electron-accepting 2,2'-bipyridine ligand during H_2 -producing reaction cycles. In a previous paper on several "Rh^I" systems $(\text{C}_5\text{Me}_5)\text{Rh}(\alpha\text{-diimine})$ [4] we drew attention to the large extent of π back donation from the metal to the acceptor ligand, which, by virtue of an "electron reservoir" [5] behaviour, seems to facilitate two-electron catalysis.

Results and discussion

Formation and electronic structure of $(\text{C}_5\text{Me}_5)\text{Ir}(\text{bpy})$

Synthesis and NMR spectroscopy. The iridium(III) precursor $[(\text{C}_5\text{Me}_5)\text{IrCl}(\text{bpy})]\text{Cl}$ was synthesized from $(\text{C}_5\text{Me}_5)_2(\mu\text{-Cl})_2\text{Cl}_2\text{Ir}_2$ and 2,2'-bipyridine [2]. Unlike the "Rh^I" analogue [4], the neutral iridium compound $(\text{C}_5\text{Me}_5)\text{Ir}(\text{bpy})$ could not be obtained intact by reduction of the precursor with potassium; tetrabutylammonium tetrahydridoborate in dry THF proved to be a more suitable reductant (Fig. 1). The electron-rich and coordinatively-unsaturated $(\text{C}_5\text{Me}_5)\text{Ir}(\text{bpy})$ is extremely air-sensitive.

Most proton and carbon NMR resonances of the bpy ligand in $(\text{C}_5\text{Me}_5)\text{Ir}(\text{bpy})$ are shifted to even lower field than those of $(\text{C}_5\text{Me}_5)\text{Rh}(\text{bpy})$ (Table 1). The effects are particularly large in aromatic solvents such as C_6D_6 and for those positions which have the largest spin density in $\text{bpy}^{\cdot-}$ (sequence: $5 \approx 4 \gg 3 > 6$) [6]. There is a significant difference, however, between the rhodium and iridium systems; in $(\text{C}_5\text{Me}_5)\text{Rh}(\text{bpy})$, the CH(4) position of 2,2'-bipyridine is the most shielded whereas in the case of the Ir analogue position 5 shows the largest high field NMR shift. In fact, a MO perturbation calculation [6] has shown a "crossing" of the spin densities at CH(4) and CH(5); a smaller Coulomb integral at the

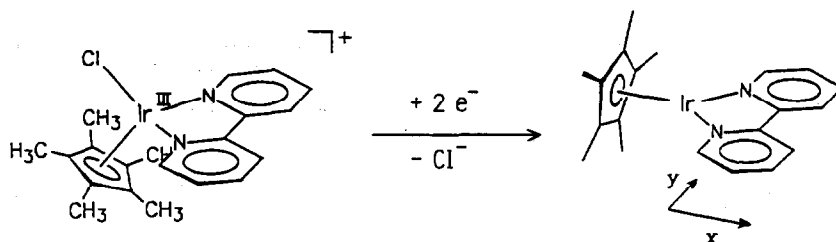


Fig. 1.

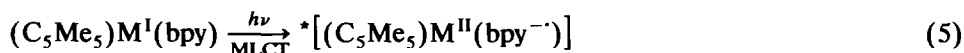
Table 1

¹H- and ¹³C-NMR data ^a for complexes (C₅Me₅)M(bpy) in C₆D₆

Nuclei	M = Rh	M = Ir
<i>(C₅Me₅)</i>		
δ _H	1.85 (s)	1.75 (s)
δ _C ^a	9.81 (q; 126.1)	9.69 (q; 126.7)
	88.91 (s)	83.52 (s)
<i>(bpy)</i>		
δ _{H(5)}	6.85 (ddd; 1.09, 6.41, 8.07)	6.16 (ddd; 1.66, 6.57, 6.90)
δ _{H(4)}	6.44 (ddd; 0.60, 7.28, 8.07)	6.71 (ddd; 1.40, 6.57, 8.80)
δ _{H(3)}	7.45 (dd; 1.09, 7.28)	7.56 (dd; 1.66, 8.80)
δ _{H(6)}	9.10 (dd; 0.60, 6.41)	8.94 (dd; 1.40, 6.90)
δ ^{C(5)}	120.73 (d; 163.4)	115.28 (d; 161.5)
δ ^{C(4)}	116.04(d; 161.9)	117.65 (d; 163.7)
δ ^{C(3)}	122.83 (d; 150.8)	123.35 (d; 158.8)
δ ^{C(2)}	136.52 (s)	141.00 (s)
δ ^{C(6)}	147.76 (d; 172.2)	147.90 (d; 178.3)

^a Coupling constants $J(^1\text{H}-^1\text{H}$ or $^{13}\text{C}-^1\text{H})$ in Hz are given in parentheses.

coordinating nitrogen (resulting from smaller electrophilic strength relative the π back donation) favours CH(5) as the centre with the highest spin density in the reduced state [6]. Given the debatable +I assignment of the metal oxidation state (see below), these NMR shifts would reflect strong contributions from low-lying metal-to-ligand charge transfer (MLCT) excited states [7] which involve the anion radical of the bpy ligand (eq. 5), indicating a sizable amount of back-donation from the (C₅Me₅)Ir^I fragment to the heterocycle.



Electrochemistry. Cyclic voltammetry of [(C₅Me₅)IrCl(bpy)]Cl was performed at scan rates between 50 and 5000 mV/s in dry and in protic (0.002 M H₂SO₄) acetonitrile/0.1 M tetrabutylammonium hexafluorophosphate (Table 2). The oxi-

Table 2

Electrochemical data for M^{III} and M^I complexes (M = Rh, Ir) ^a

M	[(C ₅ Me ₅)MCl(bpy)] ⁺				(C ₅ Me ₅)M(bpy)
	E_{pa} (ox)	E_{pc}	E_{pa}	$E_{\text{pa}} - E_{\text{pc}}$	$E_{\text{red1}} (\Delta E_{1/2})^b; i_{\text{pa}}/i_{\text{pc}}^c$
/	(free bpy ligand)				-2.57(100); 1.00
Rh	1.5	-1.36	-1.06	0.30	-2.61(80); 0.89
Ir	0.7	-1.55	-1.04	0.51	-2.82(100); 0.91
		-1.43	-1.08	0.35 (50 mV/s)	
		-1.71	-0.94	0.77 (5000 mV/s)	
+ IrH					-1.84(60); 1.00

^a From cyclic voltammetry at 100 mV/s in CH₃CN/0.1 M tetrabutylammonium hexafluorophosphate. Potentials in V vs. Fc/Fc⁺. ^b Peak potential difference in mV. ^c Peak current ratio.

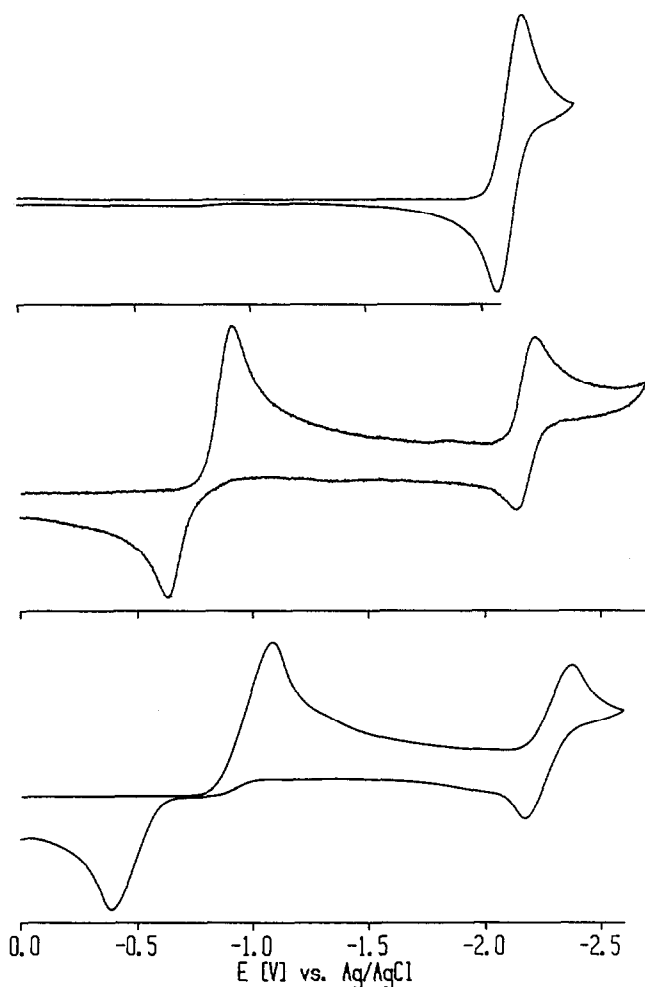


Fig. 2. Cyclic voltammograms of ligand and complexes in dry acetonitrile/0.1 M Bu_4NPF_6 , from top to bottom: bpy (100 mV/s), $[(\text{C}_5\text{Me}_5)\text{RhCl}(\text{bpy})]\text{Cl}$ (100 mV/s), $[(\text{C}_5\text{Me}_5)\text{IrCl}(\text{bpy})]\text{Cl}$ (1 V/s). Note the two-electron reduction of M^{III} cations and the one-electron reduction of the neutral complexes formed (Fc/Fc^+ ca. +0.46 V vs. Ag/AgCl).

duction of the Ir^{III} precursor ion $[(\text{C}_5\text{Me}_5)\text{IrCl}(\text{bpy})]^+$ occurs highly irreversibly at about +0.7 V vs. Fc/Fc^+ , *i.e.* at much lower potential than that for the Rh^{III} analogue (ca. +1.5 V [4]). This result suggests an oxidation of the metal-bound pentamethylcyclopentadienide, in agreement with the assignment of the long-wavelength ligand-to-metal charge transfer (LMCT) absorption bands [4].

Reduction of the Ir^{III} complex (Figs. 1 and 2) is electrochemically irreversible at a cathodic peak potential of -1.55 V vs. Fc/Fc^+ (100 mV/s). It was not unexpected that this potential for a metal-based process should be more negative for Ir^{III} than for the Rh^{III} analogue (Table 2). As has been discussed in detail for the rhodium systems [3,4], this process is a typical two electron reductive elimination $d^6 \rightarrow d^8$ with undistorted yet distinctly separated cathodic and anionic peak waves.

The mechanism involves a very rapid ECE process with facile loss of metal-bound halide ion in the course of the total two-electron reduction [3,4]. The thermally stable, though highly reactive, products of that process are the basic neutral species $(C_5Me_5)M(bpy)$ (Fig. 1). Oxidation can occur in the reverse scan as a rapid two-electron process at still negative potentials in the presence of added halide. The difference between peak potentials of the two-electron process is dependent on the cyclovoltammetric scan rate; $E_{pa} - E_{pc}$ increases with scan rate (Table 2) as reported previously for the rhodium analogue [3,4].

In agreement with the explanation offered in the case of several rhodium complexes [4], the larger peak separation observed for the iridium system than for the rhodium analogue under identical conditions suggests a stronger mixing of metal d and low-lying unoccupied ligand π orbitals in the reductively generated "M^I" complex. In other words, a large shift of E_{pc} to positive values indicates the specific stabilization of the "M^I" form due to a considerable extent of π -back donation from the metal to the heterocyclic π acceptor ligand.

A good estimate of the relative amount of π back donation can be made [4] by comparing the potentials for further reversible *one-electron* reduction of the "M^I" product complexes with that of the free bpy ligand (*cf.* Fig. 2). These single electron waves at very negative potentials show half the peak current of the M^{III/I} two-electron signals (Fig. 2).

As a rule [8], the coordination of a σ -electrophilic metal centre to a reducible ligand facilitates its reduction by increasing the electronegativity of the metal-coordinated donor centre, *i.e.* through the charge shift ligand-to-metal associated with the formation of a coordinative bond. In some instances, however, the reverse flow of electron-density *via* π -back donation or full intramolecular electron-transfer can more than compensate for the primary polarization metal ^{δ^-} /ligand ^{δ^+} , so that the complex becomes more difficult to reduce than the free π -acceptor ligand [8]. Such a situation is favoured by good metal/ligand π overlap and by either pronounced electron deficiency in the acceptor ligand or a large π electron excess on the metal donor. The latter alternative is obviously responsible for the effects observed (Fig. 2, Table 2) in case of complexes between the modestly π -accepting 2,2'-bipyridine and the very electron rich $(C_5Me_5)M$ groups. Free 2,2'-bipyridine is reduced below -2.5 V *vs.* Fc/Fc⁺ and all previously studied complexes of bpy, including those of (diolefin)M⁺ fragments (M = Rh, Ir; diolefin = 1,5-cyclooctadiene or norbornadiene [9b]) are reduced more easily than the free ligand, even if the metal centres are fairly electron rich (Table 3). Obviously, there is a large charge shift from *two* basic N lone pairs (pK_a 4.4) to the chelated metal centre.

With $(C_5Me_5)Rh$ [4], and even more so with coordinated $(C_5Me_5)Ir$, as very π electron rich metal complex fragments, the complex of bpy becomes more difficult to reduce than the free ligand (Table 3), indicating an extremely strong π electron flow from the metal centre to the unsaturated ligand. This remarkable result is in stark contrast to the "conventional" behaviour of (diolefin)M⁺ complexes of bpy [9b], which show a reduction strongly facilitated by the Rh^I and especially the Ir^I fragment (Table 3). The exchange of neutral η^4 -coordinating unsaturated ligands such as 1,5-cyclooctadiene or norbornadiene by a π electron rich anionic cyclopentadienide not only shifts the reduction potential of coordinated bpy by about 1 V (Table 3) but also changes the sequence Rh/Ir due to the stronger effects

Table 3

Potentials for the reduction of 2,2'-bipyridine and of some organometallic complexes in acetonitrile (or DMF)

Compound	E_{red} [V vs. Fc/Fc ⁺] ^a	Reference
[(bpy)Ir(cod)] ⁺	-1.55	9b
[(bpy)IrH(C ₅ Me ₅)] ⁺	-1.65	this work
(bpy)Re(CO) ₃ Cl	-1.71 ^b	10
[(bpy)Rh(cod)] ⁺	-1.72	9b
[(bpy)Cu(PPh ₃) ₂] ⁺	-1.86 ^b	11
(bpy)Mo(CO) ₄	-1.86 ^b	12
(bpy)Zn(tert-Bu) ₂	-1.86	13
(bpy)PtPh ₂	-1.94	14
(bpy)Mo(CO) ₂ (PBu ₃) ₂	-2.21 ^b	15
bpy	-2.57	4
(bpy)Rh(C ₅ Me ₅)	-2.61	4
(bpy)Ir(C ₅ Me ₅)	-2.82	this work

^a E(Fc/Fc⁺) ca. +0.46 V vs. SCE or Ag/AgCl. ^b In DMF.

displayed by the Ir systems in all instances. These results raise the question of whether a Rh^I or Ir^I formulation is an appropriate description of the metal oxidation state in (C₅Me₅)M(bpy); after sufficient intra-complex metal-to-ligand electron transfer *in the ground state* the complexes are better formulated with reduced bpy and oxidized metal (*cf.* below) [4,16]. In any case, the outstanding reduction behaviour of complexes (C₅Me₅)M(bpy) requires energetic proximity and good overlap of metal *d* and ligand π^* orbitals, which may also be responsible for the excellent “two-electron reservoir” capability and catalytic suitability [1,3] of the complexes (C₅Me₅)M(bpy) and their protonated hydride-transferring forms (eqs. 3 and 4) [1,3,17].

UV/Vis absorption spectroscopy. The Ir^{III} complex (Fig. 1) shows two broad UV/Vis absorption bands at 349 nm and at about 440 nm (weak shoulder), the interpretation of which is based on the electrochemical oxidation and reduction data. We propose that the weaker long-wavelength absorption at 440 nm is due to a (pentamethylcyclopentadienide)-ligand-to-metal charge transfer (LMCT) $\pi(\text{Cp}^*) \rightarrow d(\text{Ir}^{\text{III}})$; it is distinctly shifted to lower energies relative to the corresponding absorption for the Rh^{III} analogue [4], in agreement with a much lower oxidation potential of the Ir^{III} complex. The more intense band at 349 nm is attributed to a metal-to-(bipyridine) ligand charge transfer (MLCT) transition.

Such MLCT transitions should occur at much lower energies in the “Ir^I” complex (C₅Me₅)Ir(bpy). Figure 3 shows the spectrum together with that of the Rh analogue in toluene solution. The remarkably structured room temperature absorption spectra of the dissolved complexes with five discernible bands in the visible are not unprecedented for 5*d*⁸ metal/ α -diimine complexes with their low coordination number and high spin-orbit coupling constants; we recently reported a distinctly structured spectrum for Ph₂Pt(4,4'-bipyrimidine) in toluene solution [14].

The attribution of these bands to charge transfer transitions is based first on their intensities; the highest maxima of the complexes (C₅Me₅)M(α -diimine) have ϵ between 10³ and 10⁴ M⁻¹ cm⁻¹ (more exact values could not be obtained due to

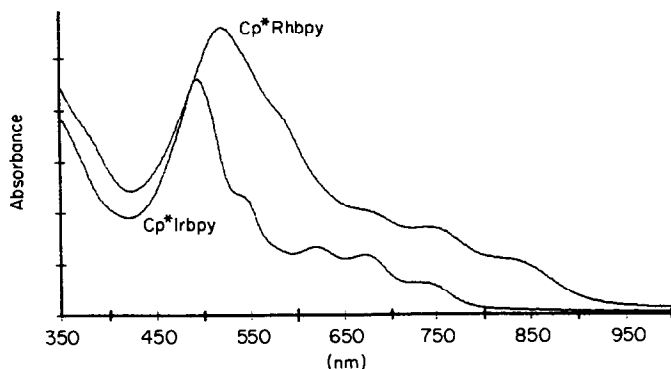


Fig. 3. Absorption spectra of complexes $(C_5Me_5)M(bpy)$, $M = Rh$ and Ir , in toluene solution ($Cp^* = C_5Me_5$). Absorbance scale different for each spectrum.

the very high sensitivity of the species). Another line of reasoning starts from the cyclic voltammetric potentials (Table 2), which reveal a difference of about 1.7 V between the anodic peak potentials of reduction and oxidation of $(C_5Me_5)Ir(bpy)$ at 50 mV/s scan rate. This value compares quite well with the 1.72 eV (1 eV = 8066 cm^{-1}) for the long-wavelength absorption maximum in acetonitrile solution (Table 4). The corresponding numbers for the rhodium analogue are *ca.* 1.5 V and 1.51 eV, illustrating the smaller frontier orbital difference in the $4d^8$ system. These rather small separations between redox potential differences and absorption energies suggest [18,19] a small intra- and inter-molecular reorganisation energy due to sizable electron delocalization between metal and (bpy) ligand; accordingly [4,19], the width at half height of the 737 nm band of $(C_5Me_5)Ir(bpy)$ is only 1000 cm^{-1} .

The very small effects of solvents (Table 4) on the charge transfer absorption energies of coordinatively unsaturated $(C_5Me_5)Ir(bpy)$ are also typical of systems with strong orbital mixing [20]. An assignment of the bands has to account for the

Table 4

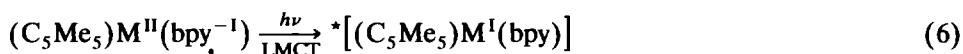
Absorption maxima λ_{max} (nm) [$\bar{\nu}_{max}$ (cm^{-1})] for $(C_5Me_5)M(bpy)$ ($M = Rh, Ir$) in the visible region

M	Solvent	Absorption maxima
Rh	toluene	520 ^a , 586sh, 674, 747, 827sh [19230 ^a , 17610sh, 14840, 13390, 12090sh]
	THF	516 ^a , 575sh, 682, 748, 830sh [19830 ^a , 17400sh, 14660, 13370, 12050sh]
Ir	toluene	494 ^a , 529sh, 617, 672, 737sh [20240 ^a , 18910sh, 16210, 14870, 13570sh]
	pentane	490 ^a , 533, 618, 670, 740sh [20430 ^a , 18760, 16180, 14920, 13510sh]
	THF	489 ^a , 534, 620, 671, 733 [20440 ^a , 18730, 16130, 14900, 13640]
	acetonitrile	491 ^a , 531sh, 610, 657sh, 720sh [20380 ^a , 18840sh, 16390, 15220sh, 13880sh]

^a Most intense maximum.

lower energies of the transitions in the rhodium system (*ca.* 1400 cm^{-1}), for the conspicuous *ca.* 1300 cm^{-1} spacing of the three long-wavelength bands, and for the 5500 cm^{-1} (Rh: 6000 cm^{-1}) difference between the highest maximum and the centre of the threefold structured band system at lower energy. The higher intensity of this long-wavelength band group in the iridium complex than of that of the Rh analogue (Fig. 3) could be due either to the effect of increased spin-orbit coupling or to the involvement of low-lying unoccupied $6p$ orbitals [21].

Fordyce and Crosby [9a] have assigned the long-wavelength bands of M^I complexes [(diolefin) $M(\text{bpy})$] $^+$ ($M = \text{Rh, Ir}$) to singlet charge transfer transitions (Rh: 485 nm; Ir: 575 nm); these absorption bands do not exhibit structure and the energy sequence $\text{Rh} > \text{Ir}$ is different from that observed here. However, the emission spectra of the diolefin complexes [9a] are structured, with a progression of about 1300 cm^{-1} typical of emissions from MLCT excited states involving (formally reduced) bipyridine ligands [22]. The result that the vibrational structuring as well as the Rh/Ir potential and absorption energy difference are *reversed* for $(\text{C}_5\text{Me}_5)\text{M}(\text{bpy})$ relative to that for the "genuine" MLCT examples [(diolefin) $M(\text{bpy})$] $^+$ suggests at least considerable orbital mixing if not a situation (eq. 6) in which the visible absorption is not due to an MLCT (5) but rather to an LMCT type transition from (intra-molecularly) reduced ligand bpy^- to an oxidized metal M^{II} [20]. Structured low intensity bands with a progression of about 1400 cm^{-1} have been observed in the same long-wavelength region for complexes of singly reduced 2,2-bipyridine [23] and similar α -diimines [24] or quinones [25].



Strong antiferromagnetic coupling between Ir^{II} and bpy^- would ensure effective diamagnetism of such a species [16,20]; the formulation in eq. 6 illustrates an approximate charge distribution and not a spin specification. All the results presented so far point to a molecular orbital situation for $(\text{C}_5\text{Me}_5)\text{M}(\text{bpy})$ in which the energies of the lowest-lying π^*_1 orbital and the (b_1 -)symmetry-related π donor orbital ($4d_{xz}$ or $5d_{xz}$) are rather similar. A stronger metal/ligand interaction in the complex of the heavier metal species results in slightly hypsochromically shifted transitions (Fig. 3, Table 4).

The π -type interacting nd_{xz} orbital is relatively low-lying in a pseudo-planar d^8 configuration [9a] and so we assign the most intense band in the visible at about 500 nm of the neutral iridium complex to a $\pi \rightarrow \pi^*$ transition which involves mixed $5d_{xz}$ and $\pi^*(\text{bpy})$ orbitals [4]. However, there are filled d orbitals of higher energy available from which dipole-allowed but overlap-disfavoured, *i.e.* weaker, transitions can occur to $\pi^*(\text{bpy})$ at low energies. In the light of the assignment by Fordyce and Crosby [9a] we associate the long wavelength band system between 600 and 800 nm to a transition involving the $5d_{z^2}$ and π^* orbitals. The alternative assignment to triplet transitions would imply a rather large singlet-triplet splitting of about 6000 cm^{-1} , which is less likely [9a] because of the apparent metal/ligand orbital mixing. Intense metal-to-ligand charge transfer bands resulting from transitions to the second lowest unoccupied MO (a_2) of bpy are observed only at relatively high energies (< 350 nm).

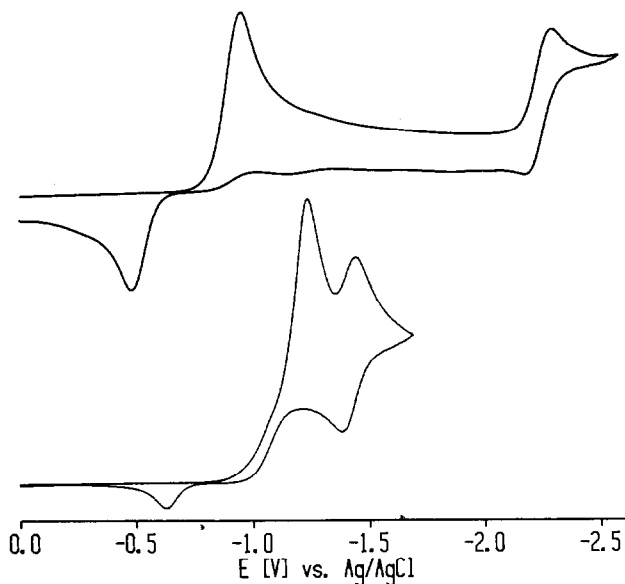
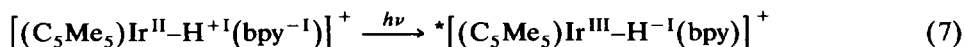


Fig. 4. Cyclic voltammogram (100 mV/s) of $[(C_5Me_5)IrCl(bpy)]Cl$ in aprotic (top) and in acidic (0.002 M H_2SO_4) acetonitrile/0.1 M Bu_4NPF_6 .

Formation and electronic structure of $[(C_5Me_5)IrH(bpy)]^+$

Cyclic voltammetry and ESR spectroscopy. The protonated form $[(C_5H_5)IrH(bpy)]^+$, obtained as previously described [2], may be compared with its conjugated base and the chloride precursor. The stability of the complex at pH 7 *in the ground state* [1] favours its description as the protonated species $[(C_5Me_5)Ir^{II}-H^+(bpy^{-1})]^+$, whereas the formation of H_2 after excitation [1,26] at pH 7 suggests a stronger contribution from the “hydridic” formulation with H^{-1} (eq. 7).



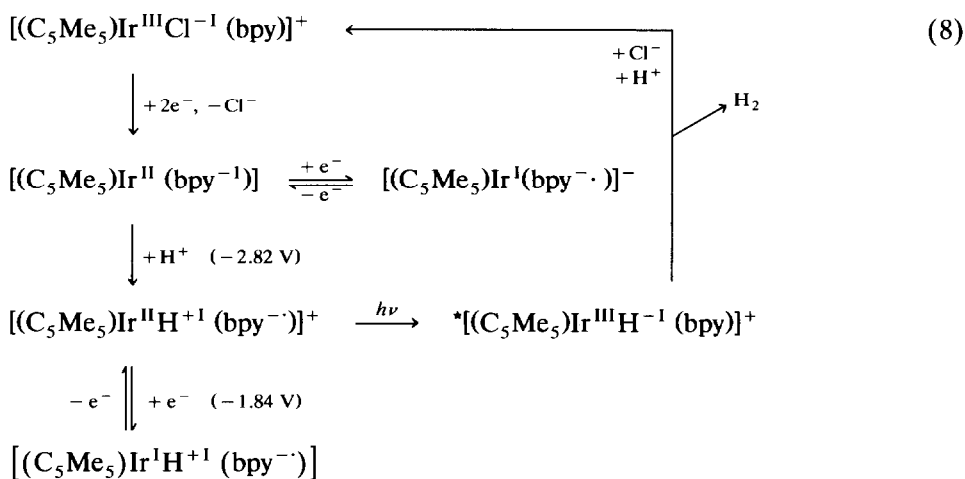
The reduction of the cation $[(C_5Me_5)IrH(bpy)]^+$ was studied by cyclic voltammetry. A reversible one-electron wave is observed at a potential which is more negative than the two-electron peak potential for *irreversible* reduction of the Ir^{III} chloride complex (Table 2). The reversibility points to the involvement of 2,2'-bipyridine in the reduction process. If instead of the pure hydride complex the chloride precursor is studied by cyclic voltammetry in slightly acidic (0.002 M H_2SO_4) acetonitrile solution, there is one large cathodic peak, followed by the reversible one-electron wave that was observed in the reduction of the pure hydride (Fig. 4).

While the cathodic shift for the hydride relative to that of the chloride-containing cation may be viewed as reflecting the higher basicity of H^{-} relative to Cl^{-} in an Ir^{III} formulation, the reversibility of the one-electron step suggests that it is not only the metal but also to a very large extent the 2,2'-bipyridine ligand which is reduced. An EPR spectrum of the reduced form $[(C_5Me_5)IrH(bpy)]^{\cdot-}$ seems to confirm this by showing a relatively narrow, unfortunately unresolved, line at g 2.003, similar to the line at g 2.001 reported for $[(diolefin)Ir^I(bpy^{\cdot-})]^{\cdot-}$ [9b]. Table 3

illustrates that the $[(C_5Me_5)IrH]^+$ fragment is thus a similar type of electrophile for bpy as the true Ir^I cation $[(cod)Ir]^+$. Staying within the Ir^{II} formulation, a difference of about 1.2 V would be quite acceptable between the reduction potentials of a base and its conjugate acid (eq. 8).

UV/Vis spectroscopy. As reported previously by Yoinou and Ziessel [2], the complex cation $[(C_5Me_5)IrH(bpy)]^+$ shows a broad long-wavelength absorption at 420 nm (ϵ 3040 $M^{-1} cm^{-1}$ [2]). Irradiation into that band in the presence of H^+ yields dihydrogen [1] in a process that we formulate as a mixed metal/bpy-to-hydrogen charge transfer (eq. 7). The Ir/bpy orbital mixing has been pointed out above, and the hydridic nature of the bound H in the excited but not in the ground state suggests a light-induced charge transfer to that atom. The possible ambiguity of metal-to-ligand charge transfer (MLCT) or ligand-to-ligand charge transfer (LLCT) *via* a connecting metal has been described before in organometallic transition and Main Group element chemistry [28,29].

Summarizing, from the studies presented, here we can formulate the reactions (eq. 8) of the iridium complexes in terms of the assignments of oxidation states shown:



While these oxidation states are the best to reflect the charge distribution it is clear that they are just crude descriptions because of the rather high degree of covalent bonding between the metal and all three ligands. Nevertheless, these assignments (eq. 8) and their experimental basis may help in the design of related homogeneous catalysts for thermal or photoinduced hydrogen production.

Experimental

Electronic absorption spectra were recorded on a Bruins Instruments Omega 10 spectrometer, the M^I compounds were studied in sealed cuvettes. 1H - and ^{13}C -NMR spectra were obtained with a Bruker AC-250 instrument. Cyclic voltammetry was performed with a PAR 273 potentiostat and a PAR 175 function generator. The three-electrode configuration consisted of a glassy carbon working electrode, a Pt wire counter electrode and a saturated Ag/AgCl electrode as reference. The ferrocene/ferrocenium couple was used as internal standard (*ca.* +0.46 V *vs.* Ag/AgCl). A 0.1 M solution of tetrabutylammonium hexafluorophosphate in dry

or protic (0.002 M H₂SO₄) acetonitrile served as electrolyte, and the concentrations of the complexes were about 10⁻³ M. Scan rates were varied between 50 and 5000 mV/s.

All reactions involving Ir^I and Rh^I were carried out under argon. Dried solvents were freshly distilled before use. Metal chloride complexes were used as purchased; the starting materials and the complexes (C₅Me₅)Rh(bpy), [(C₅Me₅)IrCl(bpy)](Cl) and [(C₅Me₅)IrH(bpy)](BPh₄) were synthesized and characterized as described previously [2–4,30].

(C₅Me₅)Ir(bpy). A suspension of 0.1 g (0.18 mmol) of yellow [(C₅Me₅)IrCl(bpy)]Cl [2] in 25 ml of dry THF was cooled to -20°C and treated with 0.1 g (0.38 mmol) of tetrabutylammonium tetrahydridoborate. After 30 minutes the purple solution was allowed to warm to room temperature and stirred for 3 h. The solids were filtered off and the filtrate was evaporated to dryness. Extraction with pentane/toluene (1/1) and crystallization from 70 ml pentane/toluene (2/1) yielded 20 mg (23%) of the deep-purple complex. Elemental analysis was not possible because of the extreme air-sensitivity of the compound. Spectroscopic data are summarized in Tables 1 and 4.

Acknowledgments

This work was supported by grants from Deutsche Forschungsgemeinschaft (SFB 270), Volkswagenstiftung and Fonds der Chemischen Industrie.

References

- 1 R. Ziessel, *Angew. Chem.*, 103 (1991) 863; *idem*, *Angew. Chem. Int. Ed. Engl.*, 30 (1991) 844; *idem*, *J. Chem. Soc., Chem. Commun.*, (1988) 16.
- 2 M.-T. Youinou and R. Ziessel, *J. Organomet. Chem.*, 363 (1989) 197.
- 3 U. Kölle and M. Grätzel, *Angew. Chem.*, 99 (1987) 572; *ibid.*, 26 (1987) 568. U. Kölle, B.-S. Kang, P. Infelta, P. Compte and M. Grätzel, *Chem. Ber.*, 122 (1989) 1869.
- 4 M. Ladwig and W. Kaim, *J. Organomet. Chem.*, 419 (1991) 233.
- 5 C. Shi and F.C. Anson, *J. Am. Chem. Soc.*, 113 (1991) 9564.
- 6 W. Kaim, *Chem. Ber.*, 114 (1981) 3789.
- 7 E.C. Alyea, J. Malito, S.D. Ernst, W. Kaim and S.J. Kohlmann, *Polyhedron*, 8 (1989) 921.
- 8 W. Kaim, *Coord. Chem. Rev.*, 76 (1987) 187.
- 9 (a) W.A. Fordyce and G.A. Crosby, *Inorg. Chem.*, 21 (1982) 1023; (b) W.A. Fordyce, K.H. Pool and G.A. Crosby, *Inorg. Chem.*, 21 (1982) 1027.
- 10 W. Kaim, H.E.A. Kramer, C. Vogler and J. Rieker, *J. Organomet. Chem.*, 367 (1989) 107.
- 11 C. Vogler and W. Kaim, *Z. Naturforsch.*, in press.
- 12 S. Ernst and W. Kaim, *J. Am. Chem. Soc.*, 108 (1986) 3578.
- 13 T. Stahl, Ph.D. Thesis, University of Stuttgart, 1992.
- 14 C. Vogler, B. Schwederski, A. Klein and W. Kaim, *J. Organomet. Chem.*, 436 (1992) 367.
- 15 S. Ernst, S. Kohlmann and W. Kaim, *J. Organomet. Chem.*, 354 (1988) 177.
- 16 M.F. Rettig and R.M. Wing, *Inorg. Chem.*, 8 (1969) 2685.
- 17 E. Steckhan, S. Herrmann, R. Ruppert, J. Thömmes and C. Wandrey, *Angew. Chem.*, 102 (1990) 445; *ibid.*, *Angew. Chem., Int. Ed. Engl.*, 29 (1990) 388.
- 18 A.B.P. Lever, *Inorganic Electronic Spectroscopy*, 2nd Edn., Elsevier, Amsterdam, 1984, p. 776.
- 19 *cf.* W. Bruns and W. Kaim, *J. Organomet. Chem.*, 390 (1990) C45.
- 20 *cf.* B. Olbrich-Deussner, W. Kaim and R. Gross-Lannert, *Inorg. Chem.*, 28 (1989) 3113.
- 21 J. Biedermann, G. Gliemann, U. Klement, K.-J. Range and M. Zabel, *Inorg. Chim. Acta*, 169 (1990) 63.
- 22 D.M. Classen and G.A. Crosby, *J. Chem. Phys.*, 48 (1968) 1853.

- 23 E. König and S. Kremer, *Chem. Phys. Lett.*, 5 (1970) 87; P.S. Braterman, J.-I. Song, C. Vogler and W. Kaim, *Inorg. Chem.*, 31 (1992) 222; T. Shida, *Electronic Absorption Spectra of Radical Ions*, Elsevier, Amsterdam, 1988, p. 197.
- 24 P.S. Braterman, J.-I. Song, S. Kohlmann, C. Vogler and W. Kaim, *J. Organomet. Chem.*, 411 (1991) 207.
- 25 A. Dei and L. Pardi, *Inorg. Chim. Acta*, 181 (1991) 3.
- 26 E.G. Megehee, T.J. Meyer, *Inorg. Chem.*, 28 (1989) 4084; D.B. MacQueen and J.D. Petersen, *Inorg. Chem.*, 29 (1990) 2313.
- 27 W. Kaim and V. Kasack, *Inorg. Chem.*, 29 (1990) 4696.
- 28 H. Kunkely and A. Vogler, *Coord. Chem. Rev.*, 111 (1991) 15.
- 29 M. Kaupp, H. Stoll, H. Preuss, W. Kaim, T. Stahl, G. van Koten, E. Wissing, W.J.J. Smeets and A.L. Spek, *J. Am. Chem. Soc.*, 113 (1991) 5606.
- 30 J.W. Kang, K. Moseley and P.M. Maitlis, *J. Am. Chem. Soc.*, 91 (1969) 5970.