C_8H_{14} where $(C_8H_{14})BH$ = 9-borabicyclo[3.3.1]nonane) in good yield.

These salts behave analogous to the corresponding bis(1-pyrazolyl)borates[4,19] and were converted to representative complexes, e.g., $R_2B(\mu\text{-tz})_2Pd(\pi\text{-}CH_2CHCH_2)$, pyrazole analogues of which have been described earlier.[10,20] Thus, replacement of the pyrazole by triazole moieties in poly(1-pyrazolyl)borates does not seem to affect the coordination behavior of the poly(triazolyl)borate anions.

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Stability Rules for d^5/d^6 Mixed-Valent Dimers. Effects from the Donor/Acceptor Capability of the Metal (Ru vs Os) and from the Occupancy of the Mediating Ligand Orbital (LUMO vs HOMO)

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Electrochemical stability constants were determined for the mixed-valent intermediates in the redox series $[(bpy)_2M(bptz)M(bpy)_2]^{4+/5+/6+}$ and $[(bpy)_2M(adc\text{-}Me^{2-})M(bpy)_2]^{2+/3+/4+}$; M = Ru, Os; bptz = 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine, adc-Me^{2-} = 1,2-diacetylhydrazido(2−). The trends observed allow us to rationalize in a consistent fashion the stability of the mixed-valence forms toward disproportionation: The equilibrium constant K_c depends on the π-donor/π-acceptor character of the metals and on the occupancy and electron population at the coordinating centers of the interacting ligand π orbital. Recent literature examples support this more practically oriented concept, which thus can be used in the design of new stable mixed-valent complexes.

Polynuclear complexes with mixed-valent metal configurations are of interest for the study of electron-transfer processes,[1] in the design of components for molecular electronics,[2] and because of their relevance to biochemically important systems.[3] An essential requirement for the investigation of mixed-valent complexes is their stability toward redox disproportionation as measured by the equilibrium constant K_c (eq 1).

$$2[M\text{-}L\text{-}M]^{n+} \rightleftharpoons [M\text{-}L\text{-}M]^{(n-1)+} + [M\text{-}L\text{-}M]^{(n+1)+}$$

$$K_c = \frac{\{[M\text{-}L\text{-}M]^{n+}\}^2}{\{[M\text{-}L\text{-}M]^{(n-1)+}\}\{[M\text{-}L\text{-}M]^{(n+1)+}\}} \qquad (1)$$

$$\log K_c = (E_1 - E_2)/0.059\ V = \Delta E/0.059\ V$$

We have recently demonstrated[4] for one particular, widely used type of complexes, viz. for dimers $[L_nRu^{II}\text{-}(\mu\text{-}A)\text{-}Ru^{III}L_n]^{5+}$,[1,5] that K_c is primarily related to the orbital overlap between the metal atoms and the π-accepting conjugated ligand bridge A; distance and orientation between the metals or the number and alternancy[5b] of metal-connecting π centers seemed to be of minor importance. A convenient, relative estimate of this overlap[4] in the case of a given ligand series can be obtained in the form of squared Hückel MO[6] coefficients c_E^2(LUMO) for the lowest unoccupied MO (LUMO) at the coordinating heteroatom (E) donor centers.

We have now extended these investigations (which are of very practical importance for the design of new mixed-valence systems)[4-7] to two further areas: We apply our previous explanation[4] to an exchange of the metal (Ru → Os) using a given π-acceptor ligand system, and we make an attempt to interpret the effects of metal and ligand exchange in mixed-valent ruthenium and osmium complexes $[L_nM^{II}\text{-}(\mu\text{-}D)\text{-}M^{III}L_n]^{3+}$ which contain a formally dianionic bridging *donor* ligand D^{2-}.[8]

As metal fragments, we employed $[M(bpy)_2]^{2+/3+}$ (M = Ru, Os; bpy = 2,2′-bipyridine), which differ from pentamminemetal fragments[1,9] $[M(NH_3)_5]^{2+/3+}$ in three ways: (i) they require *two* ligand donor centers in order to achieve coordination number 6; (ii) they contain relatively stabilized t_{2g} orbitals, resulting in rather positive redox potentials;[10] and (iii) complexes of these fragments are often soluble in aprotic media, making it possible to neglect the effects caused by hydrogen bonding.

As the acceptor ligand, we used the centrosymmetric bischelating system 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz), which is distinguished by a LUMO localized at the four tetrazine nitrogen atoms;[11] the π-donor ligand employed was the 1,2-diacetylhydrazido(2−) (adc-Me^{2-}) ligand, which can be derived from the neutral oxidized azodiacetyl (adc-Me) form. Azodicarbonyl bridging ligands[7] adc-R are unique in several ways: They contain a small, redox-active conjugated π system with four of the six centers coordinating to the two metals; the HOMO of the 1,2-diacetylhydrazido(2−) form (LUMO of the non-reduced adc-R state) has about 90% of its electron population on the coordinating heteroatom centers ($\sum c_{N,O}^2 = 0.91$);[7] substituents R at the carbon π centers can be varied from donor (NR_2, OR, alkyl) to acceptor groups (e.g. CF_3, Ph, 4-ROOC-C_6H_4),[7,12] and finally, the edge-sharing of two five-membered chelate rings in such complexes of "S-frame" ligands[11c,13e] leads to rather small metal-metal distances

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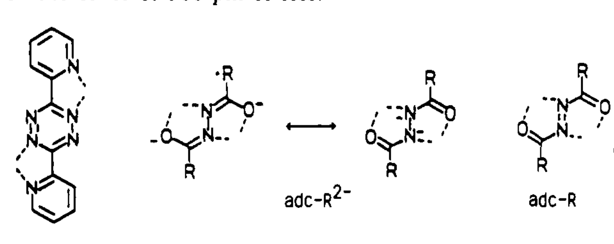
on the order of 500 pm or less.[11,13]



(2)

bptz

Experimental Section

Instrumentation and general procedures have been described previously.[4] Electronic spectra and other physical measurements of the different oxidation states of the new complexes will be discussed in detail elsewhere.[7,12,14] Hückel MO calculations[6] were carried out for adc and bibzim π systems with Coulomb integral parameters $h_N = h_O = 0.5$; all overlap integral parameters were kept at $k = 1.0$.

The starting materials bptz[15] and *cis*-M(bpy)$_2$Cl$_2$ (M = Ru, Os) were obtained via described routes.[16]

1,2-Diacetylhydrazine (adc-Me)H$_2$.[17] A 45.3-mL (479-mmol) portion of freshly distilled acetic anhydride was slowly added under cooling to 7.7 mL (159 mmol) of hydrazine hydrate. The mixture was then heated under reflux for 2 h. Water, acetic acid, and the byproduct 2,5-dimethyl-1,3,4-oxadiazole were distilled off at 150 °C bath temperature under vacuum; the residue was washed with diethyl ether and recrystallized from 100 mL of ethanol. Yield: 9.2 g (47%). Mp: 141 °C (lit. 141 °C[17]).

(μ-3,6-Bis(2-pyridyl)-1,2,4,5-tetrazine)bis(bis(2,2′-bipyridine)osmium(II)) Tetrakis(hexafluorophosphate). A 110-mg (0.19-mmol) amount of *cis*-Os(bpy)$_2$Cl$_2$ was heated with 23 mg (0.095 mmol) of bptz in 40 mL of water/ethanol (10:1) under reflux for 24 h. The cooled solution was treated with 1 g of ammonium hexafluorophosphate in 40 mL of water, and the precipitated complex was washed with water and dried under vacuum. Analytically pure material was obtained after dissolution in acetonitrile, filtration, and precipitation with diethyl ether. The dried dark green complex was isolated in 130-mg yield (75%). Anal. Calcd for $C_{52}H_{40}F_{24}N_{14}Os_2P_4$ (M_r = 1821.23): C, 34.29; H, 2.21; N, 10.77. Found: C, 34.46; H, 2.19; N, 10.60. The ruthenium analogue had been prepared in a similar manner.[11a]

(μ-1,2-Diacetylhydrazido(2−))bis(bis(2,2′-bipyridine)ruthenium(II)) Bis(hexafluorophosphate). A 100-mg (0.19-mmol) sample of *cis*-Ru(bpy)$_2$Cl$_2$·2H$_2$O and 11 mg (0.095 mmol) of 1,2-diacetylhydrazine (adc-Me)H$_2$ were heated with 20 mg (0.5 mmol) of sodium hydroxide in 40 mL of a water/ethanol mixture (5:1) under reflux for 24 h. The cooled solution was treated with 1 g of ammonium hexafluorophosphate dissolved in 40 mL of water, and the precipitated complex was dried under vacuum. Dissolution of this material in 15 mL of acetone and reprecipitation with 70 mL of diethyl ether afforded (after drying under vacuum) 106 mg (91%) of a dark purple powder. Anal. Calcd for $C_{44}H_{38}F_{12}N_{10}O_2P_2Ru_2$ (M_r = 1230.92): C, 42.93; H, 3.11; N, 11.38. Found: C, 43.60; H, 3.41; N, 11.31. The mixed-valent form, the trication, could be isolated in the pure state after oxidation with AgPF$_6$ in acetone/1,2-dichloroethane.[14b]

(μ-1,2-Diacetylhydrazido(2−))bis(bis(2,2′-bipyridine)osmium(II)) Bis(hexafluorophosphate). A mixture of 110 mg (0.19 mmol) of *cis*-Os(bpy)$_2$Cl$_2$, 11 mg (0.095 mmol) of (adc-Me)H$_2$, and 20 mg (0.5 mmol) of NaOH in 40 mL of water/ethanol (10:1) was heated to reflux for 48 h. The cooled solution was treated with 1 g of ammonium hexafluorophosphate in 40 mL of water, and the dried dark brown precipitate was then recrystallized from acetone/diethyl ether (1:4) and chromatographed on a column (alumina, Woelm A-Super I, acetone as eluent). Yield: 90 mg (77%). Anal. Calcd for $C_{44}H_{38}F_{12}N_{10}O_2Os_2P_2$ (M_r = 1230.92): C, 37.50; H, 2.72; N, 9.94. Calcd for the dihydrate (M_r = 1445.21): C, 36.57; H, 2.93; N, 9.69. Found: C, 35.92; H, 2.64; N, 9.65.

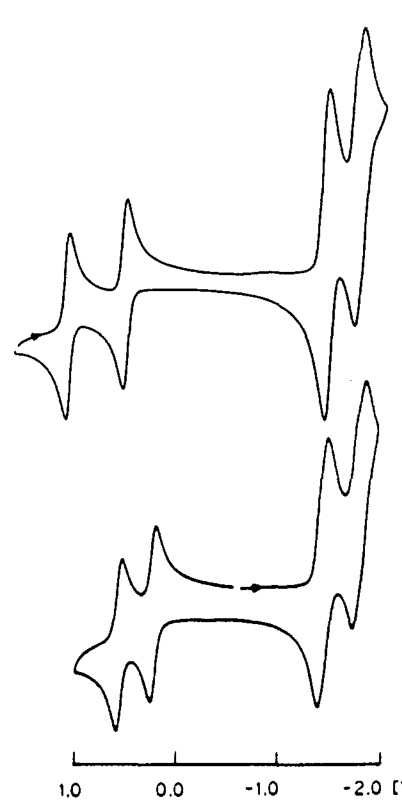


Figure 1. Cyclic voltammograms of dinuclear complexes {(adc-Me)[M(bpy)$_2$]$_2$}$^{n+}$ in acetonitrile/0.1 M tetrabutylammonium perchlorate: M = Ru (top), Os (bottom). Reductions of two pairs of bpy ligands occur between −1 and −2 V vs SCE.

Table I. Redox Potentials[a] and Comproportionation Constants K_c for Corresponding Ruthenium and Osmium Mixed-Valence (II/III) Dimers

mixed-valent form	E_{ox}	E_{red}	ΔE	K_c	ref
{[Ru(NH$_3$)$_5$]$_2$(μ-pz)}$^{5+}$	0.77	0.38	0.39	4.0×10^6	1, 5, 9
{[Os(NH$_3$)$_5$]$_2$(μ-pz)}$^{5+}$	0.32	−0.44	0.76	7.6×10^{12}	9
{[Ru(bpy)$_2$]$_2$(μ-bptz)}$^{5+}$	2.02	1.52	0.50	3.0×10^8	4
{[Os(bpy)$_2$]$_2$(μ-bptz)}$^{5+}$	1.72	1.00	0.72	1.6×10^{12}	this work
{[Ru(bpy)$_2$]$_2$(μ-bibzim)}$^{3+}$	1.06	0.77	0.39	4.0×10^6	8
{[Os(bpy)$_2$]$_2$(μ-bibzim)}$^{3+}$	0.58	0.40	0.18	1.3×10^3	8
{[Ru(bpy)$_2$]$_2$(μ-adc-Me)}$^{3+}$	0.99	0.43	0.56	3.1×10^9	this work
{[Os(bpy)$_2$]$_2$(μ-adc-Me)}$^{3+}$	0.55	0.21	0.34	5.8×10^5	this work

[a] Potentials in V vs SCE ((bpy)$_2$M systems) or in V vs NHE (pentaammine complexes). Measurements in acetonitrile ((bpy)$_2$M systems) or 0.1 M HCl (pyrazine complexes).

Results

The complexes presented in this study were synthesized in their reduced forms with regard to their metal centers (Ru^{II}, Os^{II}). The difference between the bptz- and (adc-Me)$^{2-}$-bridged complexes is obvious from the facile, ligand-based reduction of the former (4+) system.[14a] Synthesis of the (adc-R)$^{2-}$-bridged systems starts preferentially from the corresponding hydrazine[14b] although the use of the (oxidized) azodicarbonyl forms is possible in some instances.[7] While all bis(tris chelate) dimers may be formed as isomers (pairs of enantiomers and meso forms),[4] there was no evidence of a corresponding splitting of cyclic voltammetric waves.[4,8]

All complexes are oxidized in two one-electron steps with a mixed-valence intermediate, and reduction of the four bpy ligands occurs in two virtual two-electron steps, as observed previously for related systems.[4,8] Figure 1 shows the cyclic voltammograms of the adc-Me^{2-}-bridged ruthenium and osmium systems. Table I contains the redox potentials of the bis(tris chelate) complexes described here and of bis(2,2′-bipyridine)ruthenium and -osmium complexes of the dianionic 2,2′-bis(benzimidazolate) ligand bibzim^{2-};[8] also included in Table I are the data for the pyrazine-

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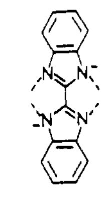
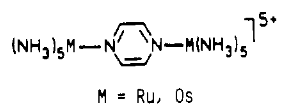
(pz-) bridged Creutz–Taube ion[1,5] and its osmium analogue.[9]



bibzim^{2-}



Discussion

In correspondence to other reported ruthenium and osmium pairs of acceptor-bridged (5+) mixed-valent complexes,[1,5,9] the two bptz systems compared here (Table I) exhibit a larger value of K_c for the Os dimer than for the Ru analogue. This result is in agreement with the rationalization given by us[4] for a series of ruthenium systems with different ligands:

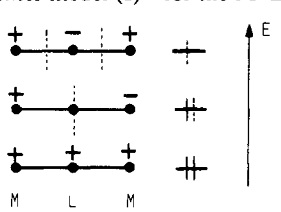
In a localized description, the initial binding of one low-valent metal center to the coordination site belonging to a conjugated π system *increases* the basicity of the free coordination centers via back-donation of π electrons to the acceptor LUMO.[18a,b] The redox potential of the *higher valent* metal atom coordinating to that free site in the mixed-valence state is thus lower than that of the first metal center, creating a potential difference ΔE and hence a sizable $K_c \gg 4$.[5] Since Os(II) is significantly more strongly back-donating than Ru(II),[5,9,18] this effect is larger for the heavier metal system.

The aforementioned argument can be reversed for those mixed-valence systems that rely on an electron-*donating*, dianionic ligand bridge with a high-lying HOMO in order to bring about communication between the two metal centers. ESR and ESCA studies[7,12,14b] of the mixed-valent (3+) ions of adc-R^{2-}-bridged systems have indeed shown a sizable metal character for those species although there may be significant contribution from an anion-radical formulation (eq 3) as demonstrated for Ru sys-

$$[M^{II}(L^{2-})M^{III}]^{3+} \leftrightarrow [M^{II}(L^{\bullet-})M^{II}]^{3+} \qquad (3)$$

tems.[7,19,20] Most notably, anisotropy and magnitude of the g factor[7] of the intermediates $[(bpy)_2Ru(adc\text{-}R)Ru(bpy)_2]^{3+}$ lie between the values for anion-radical complexes[21a,b,22c] and exclusively metal-based d^5/d^6 systems such as the Creutz–Taube ion.[21c]

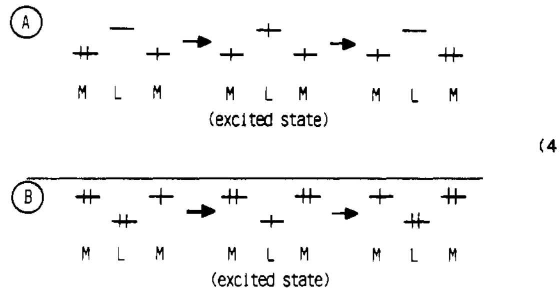
The difference between 3+ and 5+ ions can be rationalized by applying a three-center model (I)[22] for the M–L–M arrangement:



I

Whereas the 5+ ions have an allyl radical type electronic structure with vanishing spin density on the central ligand and purely metal d^5/d^6 character of the singly occupied MO (SOMO), the 3+ ions should exhibit significant spin density on the bridging ligand because the SOMO in an allyl dianion radical situation has sizable electron population on the central atom (or entity).[22c]

Corresponding to a "superexchange" mechanism (eq 4A)[1,2] for electron delocalization between metals via an *unoccupied* orbital of the bridging ligand is mechanism 4B, which describes the metal-to-metal communication using high-lying *occupied* MOs of the bridging ligand.



The 3+ ions use the latter pathway (eq 4B), which helps to explain the effects of different ligands and metals. First, it is well within our previous concept[4] that the smaller ligand adc-R^{2-} with the higher HOMO electron density $\sum c_{N,O}{}^2 = 0.91$ shows higher K_c values for its mixed-valence complexes than the larger bibzim^{2-} system with $\sum c_N{}^2 = 0.22$ (Hückel MO calculations, Coulomb integral parameters $h_N = h_O = 0.5$, all overlap integral parameters $k = 1$).

The result that the osmium systems have distinctly *smaller* K_c values than their ruthenium analogues (Table I, Figures 1 and 2) can be understood within the previously described localized model, which must involve different frontier orbitals according to (4B). Interaction of the electron-accepting *trivalent* ions with the mediating *HOMO* of the dianionic bridging ligand reduces the electron density available for binding of the second, divalent metal center. Ruthenium(III) is a far better π acceptor than osmium(III),[5,8,9,23] so that this effect is *larger* here for the lighter homologue. Reduction of electron density at the coordination site for the low-valent metal causes an increase of the redox potential for that center, so that eventually sizable ΔE and K_c values ($K_c \gg 4$) result.

Conclusion

The rationalization[4] provided initially to explain different stability constants for 5+ ions of ruthenium mixed-valence dimers with different bridging acceptor ligands is applicable in a consistent fashion to explain the effects of π-donor bridges and of metal exchange. From well-established characteristic differences of the oxidation states of Ru(II) vs Os(II) and of Ru(III) vs Os(III),[5,8,9,18,23] it could be explained that the heavier homologue with its preference for higher oxidation states causes a larger K_c in acceptor-bridged systems but a smaller K_c in donor-bridged dimers, where the ligand HOMO constitutes the exchange-supporting orbital. Additional evidence for this first rule comes from a recent study by Cayton and Chisholm, who suggested the LUMO of oxalate to be electron propagating between M(II) and M(III) centers and found a much larger K_c for M = W than for M = Mo.[24] A similar difference was established very recently for the first organometallic analogues of the Creutz-Taube ion, viz., pyrazine-bridged dimers of $[M(CO)_3(PR_3)_2]^{0/+}$, M = Mo, W.[25]

As a second rule, the orbital coefficients at the coordinating centers, i.e. at the metal/ligand "interface", contribute significantly to the size of K_c in acceptor- *and* donor-bridged complexes; these easily calculated values provide a more quantitative base than

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estimates relying on metal–metal distance and size or π alternancy of the bridging ligand.[5b] The contributions from very different kinds of metal fragments to the π overlap with one specific ligand bridge are certainly more difficult to predict; however, intensities of pertinent charge-transfer transitions can serve as useful guidelines.[25b] This approach has triggered the successful search for organometallic d^5/d^6 (μ-pyrazine) analogues of the Creutz–Taube ion that display more intense charge-transfer transitions and much larger values of K_c than the inorganic parent system.[25] Considering these more practically oriented rules for electronic coupling in addition to the well-known statistical and solvational contributions to K_c, it should thus be possible for experimentally working chemists to rationally design and synthesize new mixed-valence systems with very large stability constants.[7,25]

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Electrogenerated Chemiluminescence. 52. Binuclear Iridium(I) Complexes

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The electrochemistry and electrogenerated chemiluminescence (ECL) of $[Ir(COD)(\mu\text{-}L)]_2$, where COD is 1,5-cyclooctadiene and L is the anion of pyrazole (pz) and substituted derivatives 3-methylpyrazole (mpz) and 3,5-dimethylpyrazole (dmpz), were studied in tetrahydrofuran (THF)/0.3 M tetra-*n*-butylammonium hexafluorophosphate (TBAH). A reversible 1-electron oxidation was observed for all compounds, with the potential of the wave shifting to more negative potentials with increasing substitution of the bridging ligands. An irreversible 1-electron reduction was observed for all three compounds, attributed to a following reaction of the reduction product. The electrode reaction appears more reversible with increasing substitution of the bridging ligands, and the rate constant of the reaction following reduction of the compounds was found to decrease from 30 ± 10 s^{-1} for L = pz to 0.33 ± 0.09 s^{-1} for L = dmpz. ECL was produced upon sequential generation of Ir_2^+ and Ir_2^- by pulsing the potential of a Pt working electrode (at 20 Hz) between the anodic and the cathodic peak potentials. The emission is characteristic of the $^3B_2$ excited state of Ir_2 previously observed in the photoluminescence spectra of these compounds. ECL was also observed by oxidizing the Ir_2 compounds in solutions containing TBA oxalate.

Introduction

We report a study on the electrogenerated chemiluminescence (ECL) of $[Ir(COD)(\mu\text{-}L)]_2$, where COD is 1,5-cyclooctadiene and L is the anion of pyrazole (pz) and the substituted derivatives 3-methylpyrazole (mpz) and 3,5-dimethylpyrazole (dmpz). Much of the literature on the ECL of metal complexes is concerned with only a few types of coordination compounds such as Ru(II)[1,2] and Os(II)[3,4] tris chelates (bipyridine or phenanthroline) and molybdenum(II) halide clusters.[5,6] While many binuclear complexes containing two d^8 transition metals have been found to luminesce strongly and to have accessible oxidized and reduced states, little work has been carried out on their ECL properties. Some studies of ECL from $[Pt_2(\mu\text{-}P_2O_5H_2)_4]^{4-}$ have been reported by our group and others.[7,8] Studies of this complex were hampered by the instability of the difficult-to-characterize reduced species $[Pt_2(\mu\text{-}P_2O_5H_2)_4]^{5-}$. In this paper, we report the observation of ECL from solutions containing $[Ir(COD)(\mu\text{-}L)]_2$ alone and in the presence of oxalate anion. These complexes have attracted much attention for their novel thermal[9,10] and photochemical[11] reactivities and electrochemical[12] properties. The application of the ECL technique to this system should be useful in exploiting the electronic properties of the d^8–d^8 chromophore.

Experimental Section

The compounds $[Ir(COD)(\mu\text{-}pz)]_2$ (**1**), $[Ir(COD)(\mu\text{-}mpz)]_2$ (**2**), and $[Ir(COD)(\mu\text{-}dmpz)]_2$ (**3**), all abbreviated here as Ir_2, were prepared by the literature method.[13] Reagent grade tetrahydrofuran (THF) was predried over KOH and then twice distilled from sodium benzophenone ketyl. Tetrabutylammonium hexafluorophosphate (TBAH), used as the electrolyte, was recrystallized from EtOH followed by THF/ether. Tetrabutylammonium oxalate [$(TBA)_2Ox$)] was prepared by mixing tetrabutylammonium hydroxide and oxalic acid in a 2:1 molar ratio. The hydroscopic white solid was dried under high vacuum at room temperature for several days and stored in a drybox. The Ir_2 and oxalate reagents were kept in separate storage bulbs on the cell and added to the electrolyte solution after collection of background data. The solvent was degassed by several freeze–pump–thaw cycles (<10^{-5} Torr) before being vacuum-transferred to a storage bulb on the electrochemical cell containing dry electrolyte. Alternatively, degassed THF was stored in a He-filled drybox and added to the cell in the drybox. A one-compartment cell was used for most experiments, except the coulometric measurements, in which a three-compartment cell was employed. The three-electrode configuration was used, with a Pt disk, flag, or gauze as the working electrode, Pt foil or gauze as the auxiliary electrode, and Ag wire as the reference electrode. The silver quasireference electrode (AgQRE)

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