this range. Thus, the complexes appear to be relatively stable toward oxidation to Mn(III). Treatment of $[MnLBr]PF_6$ with Ce^{4+} in CH_3CN did cause a color change indicative of possible oxidation. In comparison, Bryan and Dabrowiak[23] reported the irreversible oxidation of $[MnMe_6[14]aneN_4]^{2+}$ in CH_3CN at -0.1 V vs. Ag/AgCl (saturated NaCl). The manganese complexes of two unsaturated macrocyclic ligands having two imine and two amide donors, $[Mn[14]12eneN_4Cl]$ and $[Mn(TPP)ClH_2O]$, exhibit Mn(III)/Mn(II) couples at approximately -0.7 V vs. Ag/AgCl (saturated NaCl) and at -0.6 V vs. $Ag/AgNO_3$, respectively.[24,25] Also, the manganese complexes of the lacunar macrocyclic ligands of Herron and Busch[26] have Mn(III)/Mn(II) half-wave potentials near -0.5 V vs. $Ag/AgNO_3$. Thus, the resistance of MnL complexes to oxidation and, indeed, the isolation of the Mn(II) complexes at all must be viewed as unusual. Of course the possibility exists that the lack of electroactivity of $[MnLX]^+$ complexes is due to large shifts because of extreme irreversibility. However, similar behavior was observed at the Pt electrode; also, the complexes are stable in air both in solution and in the solid state. Thus, it is likely that they do exhibit unusual stability. This behavior is consistent with the fact that the $[14]tetraeneN_4$ ligand is known to stabilize low oxidation states with other metals, e.g., Co(I), Cu(I), and Fe(II).

In conclusion, the chemistry of $[14]tetraeneN_4$ macrocycles has been extended to include the protonated form of the metal-free ligand and this has made possible the synthesis of Mn(II) complexes. These complexes are stable in the presence of a single halide axial ligand and are surprisingly resistant to oxidation.

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Registry No. H_4LBr_4, 100927-35-3; $[MnLF]PF_6$, 100909-21-5; $[MnLCl]PF_6$, 100909-23-7; $[MnLBr]PF_6$, 100909-25-9; $[MnLI]PF_6$, 100909-27-1; $[CuL](PF_6)_2$, 77154-14-4.

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Photosubstitution Reactions of the Ruthenium(II) Arene Complexes Ru(η^6-arene)L_3^{2+} (L = NH_3 or H_2O) in Aqueous Solution

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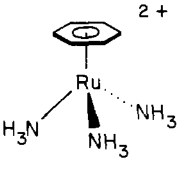
Irradiation of the ruthenium(II) complexes Ru(η^6-arene)L_3^{2+} (arene = benzene, toluene, or isopropyltoluene; L = NH_3 or H_2O) in aqueous solution leads in each case to aquation of arene as the only observable photoreaction (Ru(η^6-arene)L_3^{2+} + $3H_2O$ $\rightarrow$ $Ru(H_2O)_3L_3^{2+}$ + arene). Quantum yields ϕ_L for this process were a function of λ_{irr}, relatively low for the irradiation into the lowest energy absorption band but progressively higher at shorter wavelengths. The triammine ion Ru(η^6-C_6H_6)$(NH_3)_3^{2+}$ showed no evidence for ammine aquation or for photooxidation to Ru(III). The ϕ_L values were found to be nearly independent of whether L = NH_3 or H_2O although there are significant spectral differences between these complexes. In contrast, ϕ_L was found to be quite responsive to the nature of substituents on the arene ring. The spectral properties and potential mechanisms for arene photosubstitution are discussed.

Introduction

The work described here is concerned with the characterization of the quantitative photochemistry of a series of mono(η^6-arene) complexes of ruthenium(II), e.g.



Ib

Complexes such as Ib, which is stable toward oxidation in aqueous solution and is relatively substitution inert,[2] fall into an interface between classical "Werner type" complexes and organometallic compounds. Hexaammineruthenium(II),[3] $Ru(NH_3)_6^{2+}$ (and related Ru(II) ammine complexes),[4] as well as (benzene)(cyclopentadienyl)ruthenium(II),[5] Ru(η^6-C_6H_6)(η^5-C_5H_5)$^+$, have been investigated photochemically. In both cases, photosubstitution is a dominant reaction pathway, NH_3 being liberated from $Ru(NH_3)_6^{2+}$ and benzene from Ru(η^6-C_6H_6)(η^5-C_5H_5)$^+$. In this context, it was of interest to delineate the photoreaction properties of Ib and the similar η^6-arene ruthenium(II) complexes Ru(η^6-arene)L_3^{n+} (L = H_2O or NH_3, arene = benzene, toluene, or *p*-cymene). Of particular interest is whether the arene, which nominally occupies three coordination sites on the Ru(II) and is more robust toward thermal aquation than are the monodentate ligands, would be photolabilized preferentially to the monodentate ligands.

Some qualitative observations have been described for the photochemistry of such compounds. Bennett and Smith[6] have reported that Ru(η^6-arene)$Cl_2P(n\text{-}Bu)_3$ dissolved in another arene undergoes exchange of coordinated and solvent arenes when irradiated with UV light. Also, Taube and co-workers[7] have noted that an osmium(II) complex Os(η^6-C_6H_6)Cl_2 dissolved in water (to give, probably, Os(η^6-C_6H_6)$(H_2O)_3^{2+}$) decomposes upon UV irradiation to give free benzene as one reaction product. However, to our knowledge, no quantitative investigation of such systems has been undertaken.

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Table I. Electronic Spectra of Arene Complexes of Ruthenium(II) in Aqueous Solution[a]

complex ion	$\lambda_{max}{}^b$ $(\epsilon)^b$			
Ru(η^6-C_6H_6)$(H_2O)_3^{2+}$ (Ia)	398 (517)	312 (680)	247 (379)	
Ru(η^6-C_6H_6)$(NH_3)_2(H_2O)^{2+}$ (Id)	370 (428)	297 (650)	255 (637)	225 (756)
Ru(η^6-C_6H_6)$(NH_3)_3^{2+}$ (Ib)	356 (417)	292 (631)	257 (754)	225 (1340)
Ru(η^6-toluene)$(H_2O)_3^{2+}$ (IIa)	400 (604)	313 (764)	250 (410)[c]	232 (472)[c]
Ru(η^6-toluene)$(NH_3)_3^{2+}$ (IIb)	356 (446)	292 (612)	256 (715)	226 (1002)
Ru(η^6-*p*-cymene)$(H_2O)_3^{2+}$ (IIIa)	403 (636)	316 (727)	256 (370)[c]	233 (521)[c]
Ru(η^6-*p*-cymene)$(NH_3)_3^{2+}$ (IIIb)	360 (508)	296 (635)	256 (810)	227 (904)[c]

[a] In 0.1 N HBF_4; PF_6^- salts in each case. [b] Band maxima positions in nm; extinction coefficients in M^{-1} cm^{-1}. [c] Shoulder.

Experimental Section

Materials and Preparations. Reagent grade chemicals were used as supplied without further purification. Redistilled deionized water was used in all solution preparations. The parent compounds Ru(η^6-benzene)Cl_2 (I), Ru(η^6-toluene)Cl_2 (II) and Ru(η^6-p-cymene)Cl_2 (III, p-cymeme = *p*-isopropyltoluene) were all synthesized in high yield according to a previously published procedure[8] using ruthenium trichloride plus cyclohexadiene (Aldrich), 1-methylcyclohexa-1,4-diene (K & K) or α-phellandrene (K & K), respectively as starting compounds.

Solutions of the Triaquo Complexes. Ru(η^6-benzene)$(H_2O)_3^{2+}$ (Ia), Ru(η^6-toluene)$(H_2O)_3^{2+}$ (IIa), and Ru(η^6-*p*-cymene)$(H_2O)_3^{2+}$ (IIIa). These were prepared in situ by the following method. A 100-mg sample of I, II, or III was dissolved in water (10 mL), and the resulting yellow solution was passed through a short column filled with a strongly basic anion exchange resin in the OH^- form (Dowex 1-X-10, 50–100 mesh). This procedure led to complete removal of all ionic or coordinated chloride. The solutions so obtained were acidified with HBF_4 to generate the triaquo species. Unfortunately, attempts to prepare crystalline salts of these cationic complexes by the addition of various counterions were unsuccessful.

[Ru(η^6-benzene)$(NH_3)_3$]$(PF_6)_2$ (Ib). A 200-mg sample of I was added to a solution prepared from concentrated aqueous ammonia (1 mL) in methanol (10 mL). The resulting mixture was heated gently with stirring at 50 °C for about 1 h, during which time the complex dissolved to form a yellow solution. The methanol was then evaporated to dryness and the residue redissolved in water (10 mL). After filtration, concentrated NH_4PF_6 solution (1 mL) was added to precipitate the product. The resulting solid was recrystallized from hot water to give yellow cubic crystals with an overall yield of 76%. The derivatives [Ru(η^6-toluene)$(NH_3)_3$]$(PF_6)_2$ (IIb) and [Ru(η^6-*p*-cymene)$(NH_3)_3$]$(PF_6)_2$ (IIIb) were each prepared by an analogous procedure to give yellow crystals with respective yields of 85% and 40%.

[Ru(η^6-benzene)$(NH_3)_2$Cl]$(PF_6)\cdot 0.33NH_4PF_6$ (Ic). This compound has been prepared before,[9] but the present authors were unable to reproduce the published procedure. The preparation, however, can be easily done in the following way. A 250-mg portion of I was added to a solution containing 4 drops of concentrated aqueous NH_3 (2 mmol) in methanol (10 mL). The mixture was gently heated to 50 °C for about 30 min, whereupon the complex dissolved. After evaporation of methanol, the residue was dissolved in 0.1 M HCl (10 mL), the solution was filtered, and then saturated NH_4PF_6 solution was added to precipitate the complex as yellow needles (yield 81%). The UV–vis spectrum in 0.1 M HCl displayed λ_{max} bands at 367 (ϵ = 533 M^{-1} cm^{-1}) 308 (898), and 260 nm (675).

The aquo diammine analogue [Ru(η^6-benzene)$(NH_3)_2(H_2O)$](PF_6) (Id) was prepared as follows. A 447-mg (1.0-mmol) protion of Ic was added to a solution containing $AgBF_4$ (0.205 g, 1.05 mmol) in water (5 mL), and the resulting mixture was stirred continuously at 50 °C for about 1 h. Subsequently, the precipitated AgCl was removed by filtration, and saturated aqueous NH_4PF_6 solution (1 mL) was added to the filtrate solution. The resulting orange solution was concentrated by rotary evaporation to about 4 mL and was allowed to stand in an ice bath overnight whereupon golden, cubic crystals of the desired complex formed (yield 40%).

Analyses. Ruthenium analyses were performed in this laboratory using a method described earlier.[10] For all solid samples, C, H, N, F, and Cl determinations were carried out at the Analytische Laboratorien Malissa, Engelskirchen, West Germany, and were in agreement with the calculated values. Complex concentrations for the triaquo species in solution were determined by measuring the overall ruthenium content and assuming the molecular formula to be Ru(arene)$(H_2O)_3^{2+}$.

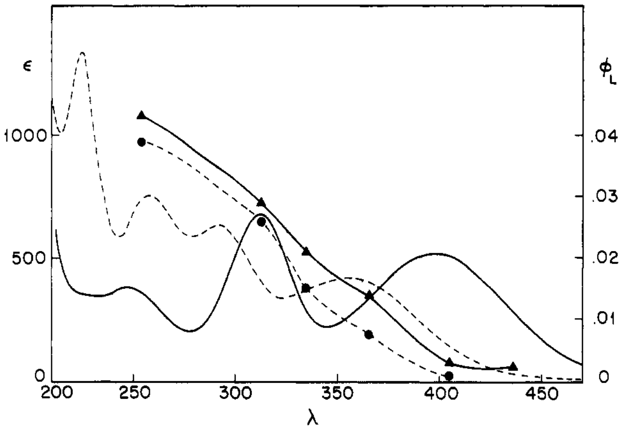

Figure 1. Spectra of the complex ions Ru(η^6-C_6H_6)$(H_2O)_3^{2+}$ (Ia, solid line) and Ru(η^6-C_6H_6)$(NH_3)_3^{2+}$ (Ib, dashed line) in 0.10 N HBF_4 aqueous solution. Also represented are the quantum yields for arene photoaquation from Ia (triangles) and Ib(dots). The lines connecting these values are drawn for illustrative purposes only.

Photochemical Procedures. Electronic spectra were obtained on a Cary 118C recording spectrophotometer equipped with a constant-temperature cell compartment. Photolyses were carried out on an optical train described in detail earlier.[11] Light intensities were determined by using ferrioxalate actinometry for irradiation wavelengths >366 nm.[12] For wavelengths ≤334 nm, the reusable heterocoerdianthrone actinometer was used.[13] Photolysis of the complexes were usually carried out in aqueous solution containing 0.1–0.001 M HBF_4. The ionic strength of the medium was always kept at 0.1 by adding appropriate amounts of $NaBF_4$. The complex concentrations were usually in the region of 10^{-3} M. Special care was taken to avoid the presence of oxygen in the photolysis solutions, and the solutions were deaerated in a Zwickel flask with chromous scrubbed argon.

The photochemical reactions for the arene complexes were monitored spectrophotometrically by following the decrease in absorbance in the region of the lowest energy absorption band (around 400 nm for the aquo complexes, around 355 nm for the ammine complexes) as functions of irradiation time. Empirical corrections for inner filter effects were applied when necessary by extrapolating calculated quantum yields to 0% conversion. Solutions of these compounds exhibited no changes in their UV–vis spectra when stored in the dark for a period of several weeks; therefore, no corrections were made for dark reactions.

Studies of pressure effects on quantum yields were carried out at the University of Frankfurt using apparatus and procedures described previously.[14]

Results and Discussion

Electronic Spectra of Complexes. Absorption spectra band maxima and extinction coefficients for the complexes described in this study are listed in Table I. In addition the spectra of Ia and Ib are illustrated in Figure 1. With the exception of the cation Ru(η^6-C_6H_6)$(H_2O)_3^{2+}$ (Ia), all aquo and ammine complexes in-

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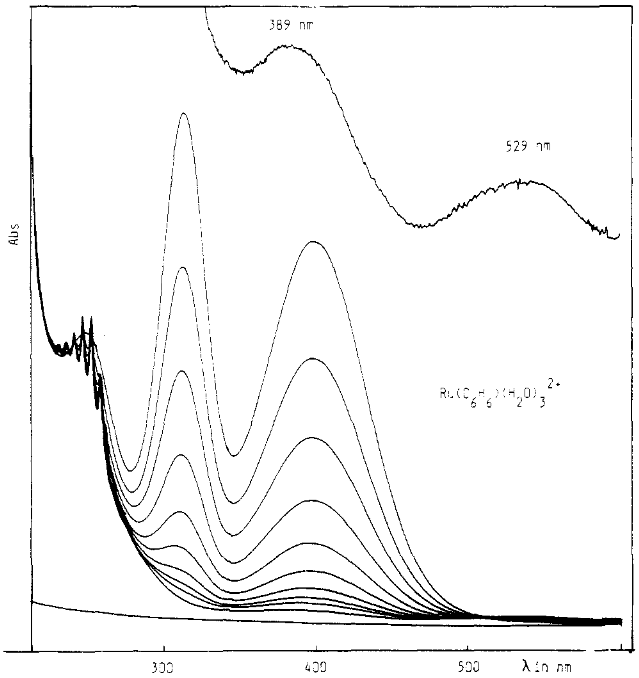

Figure 2. Progressive spectral changes observed during the exhaustive 313-nm photolysis of $Ru(\eta^6\text{-}C_6H_6)(H_2O)_3^{2+}$ in deaerated aqueous solution. The curve in the upper right hand corner represents the spectrum (expanded and offset upwards) of the final product $Ru(H_2O)_6^{2+}$.

vestigated exhibit four absorption bands in the region of 225–400 nm with extintion coefficients ranging from 400 to 1300 M^{-1} cm^{-1}. (Even for Ia, an indistinct shoulder is present at about 230 nm, which, if real, would give a total of four bands for this species as well.) The two lowest energy bands of these four are quite sensitive to the nature of the three monodentate ligands and follow the energy order $(NH_3)_3 > (NH_3)_2(H_2O) > (H_2O)_3$, consistent with ligand field strength considerations. These can be assigned qualitatively as ligand field (LF) transitions as proposed earlier.[7] This assignment is also consistent with the insensitivity of these two bands in the spectrum of $Ru(\eta^6\text{-}C_6H_6)(NH_3)_3^{2+}$ toward the nature of the solvent in methanol (λ_{max} 355 and 292 nm), acetonitrile (355 and 294 nm), or aqueous (355 and 292 nm) solutions.

Assignments for the two higher energy bands in each spectrum are less obvious. It was previously suggested[7] that the band seen at about 250 nm is a metal to ligand charge-transfer (MLCT) transition into the arene ligand. The shift of this band from 247 to 257 nm upon replacing the three aquo ligands of Ia with stronger donor NH_3 ligands to give Ib would be consistent with this assignment. However, alkyl substituents on the arene would be expected to shift an MLCT band to higher energy, and comparison of the spectra of analogous benzene, toluene, and *p*-cymeme (*p*-methylisopropylbenzene) complexes show this not to be the case (Table I). Another possible assignment for one or both of the higher bands would be as an intraligand (IL) transition localized on the benzene ring, since the spectrum of free benzene displays a structured transition at about 250 nm. However, the interaction between the metal and the π-orbitals of the ring are likely to shift such an IL transition to considerably higher energy. In this context, we consider the probable assignments of the two higher energy bands to be ligand field transitions as well (see below).

Photolysis Experiments. Irradiation of deaerated, aqueous solutions of the $Ru(\eta^6\text{-arene})(H_2O)_3^{2+}$ complexes at all wavelengths investigated in the 254–436-nm range led to major changes in the UV-visible absorption spectra (Figure 2). The disappearance of bands of the initial complexes was accompanied by appearance of new bands in the 220–260-nm region attributable to free arene. At longer wavelengths (>500 nm) small asorbance increases were observed, and exhaustively photolyzed solutions displayed a pale violet color. The final spectrum at wavelengths >260 nm (Figure 2) was found to be identical with that[15] of aqueous $Ru(H_2O)_6^{2+}$ with band maxima at 529 and 386 nm. In addition, isosbestic points persisted throughout the photolyses (e.g., at 511 nm for Ia) and their positions were independent of the irradiation wavelengths. (Note, however, that photolyses at 254 nm were carried out to only 30% conversion owing to the low intensities of the lamps.) Lastly, no pH changes ($pH_{initial}$ 3.00) were detected during the photolyses. These observations indicate that the course of reaction was uniform and that photooxidation to Ru(III) products (a process that would be reflected by pH changes) was less than experimental error limits (≤5% ϕ_{total}) at all irradiation wavelengths. The overall transformation was thus

Table II. Arene Photolabilization Quantum Yields for $Ru(\eta^6\text{-arene})(H_2O)_3^{2+}$ Complexes in Aqueous Solution[a]

	$10^2\phi_L$[c]		
λ_{irr}[b]	Ia[d]	IIa[e]	IIIa[f]
254	4.3 ± 0.3	1.9 ± 0.1	0.58 ± 0.06
313	2.9 ± 0.3	1.2 ± 0.03	0.25 ± 0.02
334	2.1 ± 0.5		
366	1.4 ± 0.05	0.41 ± 0.03	0.12 ± 0.01
405	0.29 ± 0.03	0.11 ± 0.01	0.03 ± 0.004
436	0.22 ± 0.06	≤0.04	≤0.005

[a] pH 3.00 aqueous solution. Ionic strength = 0.10 M ($NaBF_4$). [b] Irradiation wavelengths in nm. [c] Quantum yields in mol/einstein. [d] $Ru(\eta^6\text{-}C_6H_6)(H_2O)_3^{2+}$. [e] $Ru(\eta^6\text{-toluene})(H_2O)_3^{2+}$. [f] $Ru(\eta^6\text{-}p\text{-cymene})(H_2O)_3^{2+}$.

$$Ru(\eta^6\text{-arene})(H_2O)_3^{2+} + 3H_2O \xrightarrow{h\nu} \text{arene} + Ru(H_2O)_6^{2+} \quad (1)$$

For the di- and triammine complexes $Ru(\eta^6\text{-}C_6H_6)(NH_3)_2(H_2O)^{2+}$ (Id) and $Ru(\eta^6\text{-}C_6H_6)(NH_3)_3^{2+}$ (Ib), similar spectral changes were observed for the earlier stages of the reaction and isosbestic points persisted for about 30% of the reaction as defined in terms of absorbance decreases of the lower energy bands for the starting materials. After exhaustive photolysis at 313 nm, the product spectra exhibited the weak absorption bands characteristic of $Ru(H_2O)_6^{2+}$. The pattern of spectral changes indicate that the primary photochemical pathway for either Id or Ib is the release of benzene to give $Ru(NH_3)_2(H_2O)_4^{2+}$ and $Ru(NH_3)_3(H_2O)_3^{2+}$, respectively, followed by the action of these products as inner filters and the resulting photoaquation of the coordinated ammines, e.g.

$$Ru(\eta^6\text{-}C_6H_6)(NH_3)_3^{2+} + 3H_2O \xrightarrow{h\nu} Ru(NH_3)_3(H_2O)_3^{2+} + C_6H_6 \quad (2)$$

$$Ru(NH_3)_3(H_2O)_3^{2+} + 3H_2O \xrightarrow[\text{(several steps)}]{h\nu} Ru(H_2O)_6^{2+} + 3NH_3 \quad (3)$$

In the initial stages of the photolysis, pH changes in the weakly acidic (pH 3.00) solutions were very small or nonexistent and an upper limit for the quantum yield for photoaquation of the Brønsted base NH_3 from either Ib or Id could be calculated as about 5×10^{-4} mol/einstein. (Similarly, the quantum yield upper limit for photooxidation was also 5×10^{-4}.) Furthermore, the photolysis of Ib led to intensity decreases but no shift in the absorption maxima attributed to the lower energy LF transitions, so it can be concluded that photoaquation of NH_3 from Ib to give Id does not compete significantly with the photoaquation of benzene. The failure of the monodentate ammine ligands to undergo photolabilization in this case contrasts to the photoreaction behavior of $Cr(\eta^6\text{-}C_6H_6)(CO)_3$ and its derivatives, the photoreactions of which are largely dominated by CO labilization.[16]

The quantum yields (ϕ_L) for arene labilization from Ia, IIa, IIIa, Ib and Id summarized in Tables II and III show a significant dependence of ϕ_L on the excitation wavelength. In each case, ϕ_L was found to be quite small in the region of the lowest energy LF absorption band and increased progressively at higher excitation

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Table III. Quantum Yields for Benzene Photolabilization from $Ru(\eta^6\text{-}C_6H_6)(NH_3)_3^{2+}$ and from $Ru(\eta^6\text{-}C_6H_6)(NH_3)_2(H_2O)^{2+}$[a]

	$10^2\phi_L$[c]	
λ_{irr}[b]	Ib[d]	Id[e]
254	3.90 ± 0.15	3.51 ± 0.09
313	2.60 ± 0.08 (1.43 ± 0.05)[f] (1.05 ± 0.04)[g]	2.16 ± 0.08
334	1.50 ± 0.08	
366	0.76 ± 0.04	0.57 ± 0.02
405	0.08 ± 0.01	0.18 ± 0.01
436		0.058 ± 0.004

[a] Photolyses in pH 3.0 aqueous solution except where noted. Ionic strength = 0.10 M ($NaBF_4$) at 25 °C. [b] Irradiation wavelength in nm. [c] Quantum yield in mol/einstein. [d] $Ru(\eta^6\text{-}C_6H_6)(NH_3)_3^{2+}$. [e] $Ru(\eta^6\text{-}C_6H_6)(NH_3)_2(H_2O)^{2+}$. [f] 0.9 M acetonitrile. [g] 3.2 M acetonitrile (18% by volume).

energies (Figure 1). Thus, the reactive state in each case is apparently an upper state or is a nonspectroscopic state not efficiently accessible by irradiation into the lowest energy absorption band.[17]

It is notable that the ϕ_L values proved to be quite sensitive to substituents on the arene ring but not to the nature of the monodentate ligands. Despite the relative independence of the absorption spectra to the presence of alkyl substituents on the arenes, the more substituted metalloarenes were significantly less photoactive. In contrast, the very similar ϕ_L values measured for Ia, Ib, and Id indicate a much smaller sensitivity of ϕ_L to the nature of the three monodentate ligands although in these cases the absorption spectra varied considerably.

The effects of medium on ϕ_L values were briefly examined by carrying out the 313-nm photolysis of Ib in the presence of added acetonitrile (acn). Although acn forms quite stable complexes with Ru(II) ammines, e.g. $Ru(NH_3)_5acn^{2+}$,[17] acn added to the aqueous solutions served to suppress the photolabilization of benzene substantially. For example, addition of acn at concentrations representing a molar fraction less than 10% decreased ϕ_L to about 40% of its value in purely aqueous solution (Table III). Given that the acn electronic states should all lie at energies substantially higher than those of Ib, it is unlikely that these effects result from energy transfer (i.e. electronic quenching) but instead may reflect reactivtiy differences between acn or H_2O in trapping a key excited state or intermediate. Since this system appears to react from a short-lived, upper excited state, a logical suggestion would be that acetonitrile specifically solvates Ib in the mixed solvent and that the reactivity differences are the result of differences between solvent cage acn and H_2O in their abilities to react with the relevant excited state or key intermediate (see below).

Also examined were the ϕ_L values for Ia in aqueous solution as a function of applied hydrostatic pressure. Systematic, but very modest, decreases in ϕ_L resulted as the pressure was increased from 1.0 MPa to 200 MPa (roughly 2000 atm), the overall ϕ_L change for this pressure range being about 10%. The apparent volume of activation $\Delta V^{\ddagger}$(apparent) derived from a plot of ln $(\phi_L/(1 - \phi_L))$ vs. P[14] was +1.1 ± 0.4 cm^3/mol.

Figure 3 represents a simplified orbital diagram for Ib constructed from the C_{3v} fragment $Ru(NH_3)_3^{2+}$ plus C_6H_6. σ bonding to the three ammines splits the ligand field orbitals into the e (d_{xz}, d_{yz}), which are antibonding σ^*_{MA} (A = NH_3), and a_1 (d_{z^2}) plus e′ (d_{xy}, $d_{x^2-y^2}$), which are essentially nonbonding or are weakly σ^*_{MA} owing to poor overlap. Interaction with the benzene π orbitals leads to σ-, π-, and δ-bonding interactions,[19] the e′ ligand field orbitals becoming δ^b and the e orbitals now having both σ^*_{MA} and π^*_{ML} character, while the a_1 (d_{z^2}) metal orbital should mix with the lowest energy a_1 benzene ring orbital plus the a_1 (p_z) of the metal to become weakly σ^*_{ML}. With this type of splitting, the LF orbital (state) transitions can be represented as $a_1 \rightarrow e$ ($^1A_1 \rightarrow {}^1E$) and $e' \rightarrow e$ ($^1A_1 \rightarrow {}^1E$, $^1A_1$, $^1A_2$), i.e. a total of four electronic transitions consistent with the four bands in the electronic spectra. The lowest energy singlet state resulting from the a_1 (σ^*_{ML}) $\rightarrow$ e (σ^*_{MA}, π^*_{ML}) orbital transition might be expected to be less labile toward benzene labilization than those states resulting from e′ (δ^b_{ML}) $\rightarrow$ e (π^*_{ML}, σ^*_{MA}) excitation. This may explain the λ_{irr} dependence of the arene photolabilization where ϕ_L values at the longer wavelengths are only a small fraction of those resulting from excitation at the second asorption band or higher energy. However, the failure of the lower energy excitation to labilize NH_3 remains surprising given the marked photolability of aqueous $Ru(NH_3)_6^{2+}$ when irradiated at wavelengths corresponding to the lowest energy LF absorption bands (ϕ_A = 0.27 at λ_{irr} 405 nm).[3] One possible explanation may be that the a_1 orbital should be somewht σ antibonding with respect to the ruthenium ammine bands, therefore the $a_1 \rightarrow e$ excitation does not strongly perturb the metal–ammine bonding.

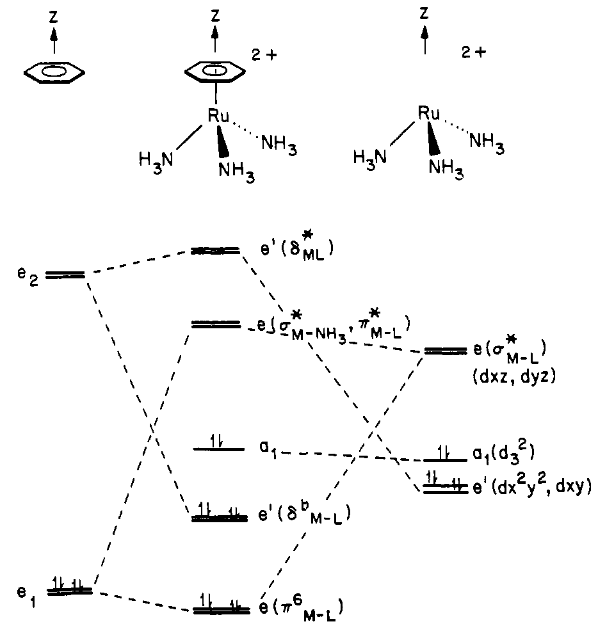

Figure 3. Qualitative orbital diagram for $Ru(\eta^6\text{-}C_6H_6)(NH_3)_3^{2+}$. C_{3v} symmetry was assumed except that e orbitals are labeled e and e′, respectively, if they correlate to the e_1 and e_2 orbitals of C_{6v} symmetry.

The mechanism of arene photolabilization has been the subject of investigation for both the $Cr(CO)_3(\eta^6\text{-}C_6H_6)$ and the $M(\eta^6\text{-}C_6H_6)(\eta^5\text{-}C_5H_5)^+$ (M = Fe or Ru) systems. For the former, arene labilization apparently is preceeded by CO photodissociation and is not a primary photoreaction.[16] For the latter systems there is no evidence of cyclopentadienyl labilization, thus the primary photoreaction appears to involve the arene.[5] The same must be the case for $Ru(\eta^5\text{-}C_6H_6)(NH_3)_3^{2+}$ given that no NH_3 photoaquation was observed from this ion. Furthermore, the close parallel between the ϕ_L values for Ia and Ib at all wavelengths investigated strongly implies a parallelism in the photoreaction mechanisms for these two complexes. In addition, the substituent effects noted here for Ia, IIa, and IIIa (namely that alkyl groups on the arene decrease ϕ_L) are consistent with the substituent effects noted by Mann and co-workers for the $M(\eta^6\text{-}C_6H_6)(\eta^5\text{-}C_5H_5)^+$ ions,[5c] thus it appears likely that analogous mechanisms would be responsible for the arene photolabilizations in both types of systems. Mann and co-workers also noted[5b] that, for the M-

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(17) (a) It was suggested by a reviewer that the quantum yield dependences on excitation wavelength were similar to those seen for solvent cage effects. Although we cannot at this point exclude such an explanation, the cage effect argument would imply a dissociative excited state. The excitation energy in excess of the arene–ruthenium bond energy becomes translational, allowing the solvent caged pair $Ru(NH_3)_3^{2+}$–arene to diffuse apart in competition with recombining. It is our opinion that such competition should be more sensitive to pressure effects than was observed here.[17b] (b) DiBenedetto, J. Ford, P. C. *Coord. Chem. Rev.* **1985**, *64*, 361–382.

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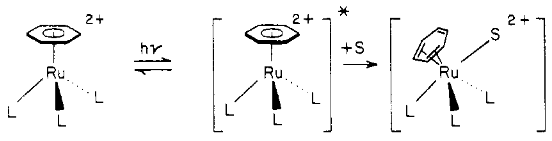
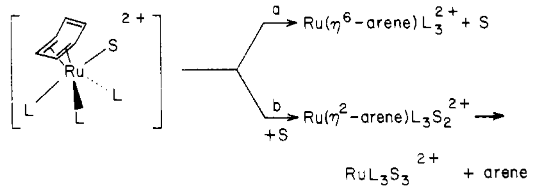
$(\eta^6C_6H_6)(\eta^5\text{-}C_5H_5)^+$ ions, ϕ_L values (313 nm excitation) are markedly medium-dependent, being significantly larger in more nucleophilic solvents. For Ib quantum yields were reduced even in the presence of relatively small concentrations of CH_3CN in the aqueous solution.

In these contexts, a potential mechanism for this reaction would be for the excited state, having a distorted metal-arene bond, to undergo competitive deactivation to the ground state (or less reactive lower energy states) or reaction with solvent to give an intemediate species such as a solvated η^4-arene, e.g.


(4)

This intermediate would also have the option of reacting further to give the fully solvated product or to lose S to regenerate the starting complex, e.g.


(5)

Analogous mechanisms have been proposed for the mechanisms for the thermal exchange of solution and coordinated arenes.[20]

The overall quantum yield for eq 4 would be determined by the branching efficiencies at each stage of this of this mechanism. More nucleophilic solvents would therefore be expected to favor arene labilization. Alkyl substitution perhaps would inhibit solvent attack in eq 4 owing to steric effects as well as make the arene a stronger nucleophile, better able to displace S from the η^4 intermediate. Both effects would lower the efficiency of photolabilization as observed. The ΔV^*(apparent) measured for such a mechanism would reflect the volume differences between the transition states of competing pathways (e.g., eq 5a or 5b), leading to starting material or to product. The small value of this parameter suggests that the volume profile for steps leading back to starting material or going on to products involve comparable ΔV^* values. For eq 5a and 5b, this would be consistent with both such pathways being essentially interchange processes between ligands in the first and second coordiations spheres thus having ΔV^* values of the same sign and similar magnitudes (probably small).

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Registry No. I, 35796-48-6; Ia, 75701-06-3; Ib, 68193-71-5; Ic, 66219-75-8; Id, 100928-23-2; II, 100928-21-0; IIa, 100928-15-2; IIb, 100928-18-5; III, 100928-22-1; IIIa, 100928-16-3; IIIb, 100928-20-9.

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The Tungsten-Tungsten Triple Bond. 12.[1] Bis(1,3-diaryltriazenido)bis(dimethylamido)diethylditungsten (M≡M) Compounds

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anti- and *gauche*-$W_2Et_2(NMe_2)_4$ react with 1,3-diaryltriazenes, ArNNNHAr, where Ar = phenyl (Ph) and *p*-tolyl (*p*-tol), in hydrocarbon solvents to give $W_2Et_2(NMe_2)_2(ArN_3Ar)_2$ compounds in three isomeric forms, A, B, and C. Isomers A and B are formed kinetically from *gauche*- and *anti*-1,2-$W_2Et_2(NMe_2)_4$, respectively. With time, isomer A is converted to isomer B, which reacts further to give an equilibrium mixture of B and C. The isomer B, where Ar = Ph, and isomer C, where Ar = *p*-tol, have been characterized by single-crystal X-ray studies. In both isomers each tungsten atom is coordinated to three nitrogen atoms and one carbon atom in a roughly square-planar manner and united to the other tungsten atom by a W≡W bond. For isomer B (Ar = Ph) the W≡W bond is unbridged, W-W = 2.304 (1) Å, while for C (Ar = *p*-tol) there is a pair of cis-bridging triazenido ligands, W-W = 2.267 (1) Å. On the basis of the observed solid-state structures and NMR studies of the reaction between $W_2Et_2(NMe_2)_4$ and 1,3-diaryltriazenes, a reaction sequence accounting for the kinetic sequence of events is proposed. Crystal data follow for the compounds $W_2Et_2(NMe_2)_2(ArN_3Ar)_2$. For Ar = Ph, at -159 °C: a = 19.504 (5) Å, b = 8.650 (1) Å, c = 19.385 (5) Å, Z = 4, d_{calcd} = 1.841 g cm^{-3}, space group *Pbcn*. For Ar = *p*-tol, at -161 °C: a = 12.728 (5) Å, b = 13.990 (7) Å, c = 21.274 (10) Å, β = 98.17 (2)°, d_{calcd} = 1.705 g cm^{-3}, space group $P2_1/c$.

Introduction

Following our discovery[2,3] of dinuclear reductive-elimination reactions involving molybdenum, eq 1 and 2 where R = a β-hydrogen-containing alkyl ligand, we were hopeful that analogous procedures could be used for the synthesis of quadruply bonded (W-W) carbamates and triazenides of tungsten.

$$Mo_2R_2(NMe_2)_4 + 4CO_2 \rightarrow Mo_2(O_2CNMe_2)_4 + \text{alkene} + \text{alkane} \quad (1)$$

$$Mo_2R_2(NMe_2)_4 + 4ArNNNHAr \rightarrow Mo_2(ArN_3Ar)_4 + 4HNMe_2 + \text{alkene} + \text{alkane} \quad (2)$$

However, this did not prove to be the case,[2,4] and the reactions involving $W_2R_2(NMe_2)_4$ compounds have proved much more complex. We describe here our studies of the initial steps of the reaction between $W_2Et_2(NMe_2)_4$ and 1,3-diaryltriazenes, which are well-behaved in yielding isolable compounds of formula $W_2Et_2(NMe_2)_2(ArN_3Ar)_2$, where Ar = Ph and *p*-tol. In a subsequent paper we shall describe how further reactions with triazenes and carbon dioxide proceed.

Results and Discussion

Synthesis. $W_2Et_2(NMe_2)_2(ArN_3Ar)_2$ compounds, I (Ar = Ph) and II (Ar = *p*-tol), can be prepared by mixing $W_2Et_2(NMe_2)_4$ and the 1,3-diaryltriazenes in hydrocarbon solvents at room

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