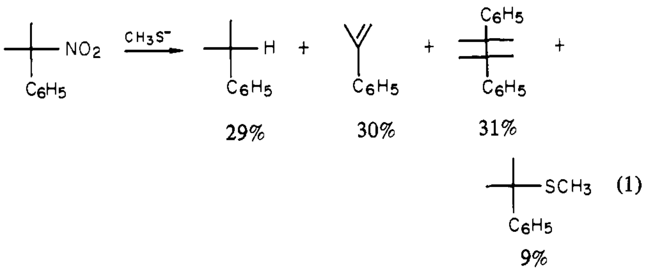
example (using the least successful example reported[3b]), yields a mixture of products (NMR analysis) when α-nitrocumene is treated with sodium thiomethoxide in HMPA (eq 1), while only



the reduction product, cumene, 79% (Table I, reactions 46,47), is produced by using tri-*n*-butyltin hydride in benzene. The difference in the reactions is undoubtedly due to the ease of hydrogen transfer with the tri-*n*-butyltin hydride compared to the less facile transfer reactions with thiomethoxide. In the latter case, the relatively stable cumyl radical underwent radical–radical combination and disproportionation in preference to hydrogen abstraction.[3b]

Further work on the alternative mechanisms available for the reagent trialkyltin hydride is presently under investigation.

Photooxidation of (2,2′-Bipyridine)(3,4-toluenedithiolato)platinum(II) following Ligand-to-Ligand Charge-Transfer Excitation

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In mixed-ligand complexes it is possible that electronic transitions occur involving charge-transfer (CT) from one ligand to another. Absorption bands corresponding to such ligand-to-ligand CT transitions (LLCT) may be observed at low energies if one ligand is reducing and the other is oxidizing or, in other terms, if one ligand has high-lying filled orbitals and the other low-lying empty orbitals. To our knowledge there are only four reports on the existence of such absorption bands. Two are dealing with complexes of closed-shell metals [Be(II)[1] and Zn(II)[2]], while two examples are known for transition metals [Fe(II)[3] and Ni(II)[4]], the most elaborate being the last one by Miller and Dance.[4] We describe here emission and reactivity of a LLCT excited state. Another point of interest of the present study is a certain relationship between LLCT transitions and intervalence or mixed-valence CT transitions of hetero-binuclear metal complexes.[5] In both cases an optical electron transfer occurs between different parts of a molecule which are separated by intervening atoms.

The complex (bpy)Pt^{II}(tdt) where bpy and tdt^{2-} denote 2,2′-bipyridine and 3,4-toluenedithiolate dianion was prepared by boiling (bpy)PtCl$_2$[6] and 3,4-toluenedithiol in ethanol and obtained analytically pure by extraction with acetone. The absorption spectrum (Figure 1) of (bpy)Pt(tdt) shows an intense long-wavelength absorption which is strongly solvent dependent [λ_{max} (C$_2$H$_5$OH) 558 nm (ϵ 3900); λ_{max} (CHCl$_3$) 610 nm, (ϵ = 4100)].

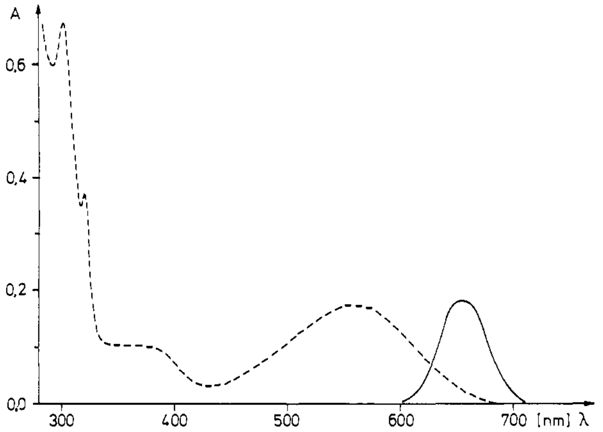

Figure 1. Electronic absorption and emission spectrum of (bpy)Pt(tdt) in ethanol. Absorption (---): 4.9 × 10^{-5} M complex concentration, 298 K, 1-cm cell; emission (—): 77 K, λ_{exc} = 546 nm, intensity in arbitrary units, not corrected.

This absorption band does not have a counterpart in the spectrum of (bpy)PtX$_2$ with X = Cl, Br, I.[7] The lowest energy absorptions of these complexes which are of the CT [Pt(II) → bpy] type occur at much higher energies. Following the arguments of Miller and Dance[4] the ground state of (bpy)Pt(tdt) is best described as a Pt(II) complex containing a neutral bipyridyl, which shows the characteristic $\pi\pi^*$ intraligand absorptions[7] at 304 and 320 nm, and a dithiolate dianion as ligands. Consequently, the long-wavelength band, which causes the solvochromic behavior of the complex, is assigned to a LLCT transition from the dithiolate to the bipyridyl. When (bpy)Pt(tdt) was excited with light of different wavelengths (366, 436, 546 nm) in an ethanol glass at 77 K, a strong red emission was observed (Figure 1). We assign this emission which centers at 654 nm to the transition from the LLCT excited state to the ground state.

At room temperature in an ethanol solution the emission of (bpy)Pt(tdt) could not be observed, but the solution was stable to light. However, in solutions of CHCl$_3$ the complex decomposed upon irradiation. At 577-nm irradiating wavelength the disappearance quantum yield was ϕ = 0.03. In analogy to other complexes which are photooxidized in CHCl$_3$,[8-10] we assume that in the LLCT excited state the platinum complex transfers an electron to CHCl$_3$ in the primary photochemical step according to

$$[(\mathrm{bpy})\mathrm{Pt}(\mathrm{tdt})]^* + \mathrm{CHCl_3} \rightarrow [(\mathrm{bpy})\mathrm{Pt}(\mathrm{tdt})]^+ + \mathrm{Cl}^- + \cdot\mathrm{CHCl_2}$$

Evidence for this assumption was obtained by the results of a low-temperature photolysis. Upon irradiation of (bpy)Pt(tdt) in a toluene/CHCl$_3$ glass (50:50) at 77 K the color faded. Simultaneously an ESR signal developed which disappeared on heating the sample. This signal with g = 2.0093, which is close to the free-electron value, is consistent with a ligand-centered radical.[11] Since the tdt^{2-} ligand is easily oxidized,[12] the primary photooxidized complex should contain the tdt$^-$ radical.[13] The resulting complex cation [(bpy)Pt^{II}(tdt$^-$)]$^+$ is apparently not stable

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but decomposes to unidentified products in a secondary reaction.

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Radical Anions of Triptycene Bis- and Tris(quinones)[1]

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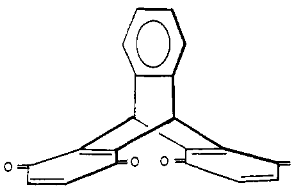
The formation of radical ions upon reduction of **1** and **2** has been investigated in MeCN and Me_2SO solutions by ESR spectroscopy. We were interested in ascertaining if both radical mono- and trianions could be detected and if their unpaired electrons are delocalized over all quinone rings, since the first reduction potential of **1** is reported to be considerably lower than the reduction potential of triptycene monoquinone.[2] We were surprised to observe, in addition to $\mathbf{1}^{-}\cdot$ and $\mathbf{1}^{3-}\cdot$, an intermediate paramagnetic reduction product with a well-resolved ESR spectrum which appears to be the diradical ($\cdot\mathbf{1}^{2-}\cdot$), while for **2** at least three discrete paramagnetic radical anions can be detected by ESR spectroscopy.



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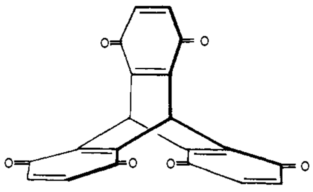

2

Radical Monoanion of 1. Electrolytic reduction at Hg or Pt of **1** in MeCN or Me_2SO gave initially the 1:4:6:4:1 pentet of Figure 1a ($a^H = 1.10$ G, $g = 2.00506$ in Me_2SO). Occasionally a further hyperfine splitting of $\simeq 0.05$ G by two hydrogens was observed. This species does not have the electron delocalized over both rings, because cooling the MeCN solution resulted in selective line broadening of the second and fourth peaks. At -55 °C these peaks were essentially unobservable, and a ~1:4:1 triplet of sharp lines was observed (warming to 25 °C restored the 1:4:6:4:1 pentet). The hydrogen atoms of the bis(quinone) rings of $\mathbf{1}^{-}\cdot$ are time averaged by electron migration for which an energy barrier of $\Delta H^{\ddagger} = 6.2$ kcal/mol ($\Delta S^{\ddagger} = -7$ eu) was calculated from the selective line broadening observed between -50 and 0 °C. Dilution of solutions giving spectrum **1a** by 200-fold did not affect the line widths or intensities of the 1:4:6:4:1 pentet. The pentet was not immediately destroyed by exposure to oxygen.

Diradical Dianion of 1. Continued electrolysis of **1** in Me_2SO ($Bu_4N^+ClO_4^-$) at a Hg pool or Pt electrode resulted in the appearance of a 1:2:1 triplet, which was not time averaged with the pentet of $\mathbf{1}^{-}\cdot$. After a sufficiently long period of electroreduction, the pentet disappeared completely to give the spectrum as shown in Figure 1b ($a^H = 2.45$ (Me_2SO), 2.40 (MeCN) G) with a g value equal to that of $\mathbf{1}^{-}\cdot$. The triplet of Figure 1b would be consistent with a diradical structure if $J \ll a_H$ (i.e., no correlation between the electrons).[3,4] Time averaging of the two rings in the diradical state by a concerted migration of the two electrons would be highly improbable, and up to 100 °C the spectrum was a sharp 1:2:1 triplet with lines not appreciably broader than for $\mathbf{1}^{-}\cdot$. Exchange of the two electrons by way of the dianion in which both electrons are in the same quinone ring does not occur rapidly. Frozen Me_2SO solutions of the species responsible for the 1:2:1 triplet still gave the 1:2:1 hyperfine splitting, and no $\Delta m = 2$ transition could be observed. The species responsible for the 1:2:1 triplet was observed in the presence or absence of excess base, the presence or absence of K^+, and was not converted to another species by dilution. The diradical reacted with an excess of the bis(quinone) to regenerate $\mathbf{1}^{-}\cdot$ but was stable to molecular oxygen. The biradical was more easily observed at very low free quinone concentrations. Thus electrolysis in Me_2SO-H_2O (80:20), MeCN-H_2O (85:15), MeCN-MeOH, or MeCN-Et_3N mixtures either gave rise to spectrum 1b as the initial species or greatly shortened the period required for the complete conversion of $\mathbf{1}^{-}\cdot$ to $\cdot\mathbf{1}^{2-}\cdot$.[5]

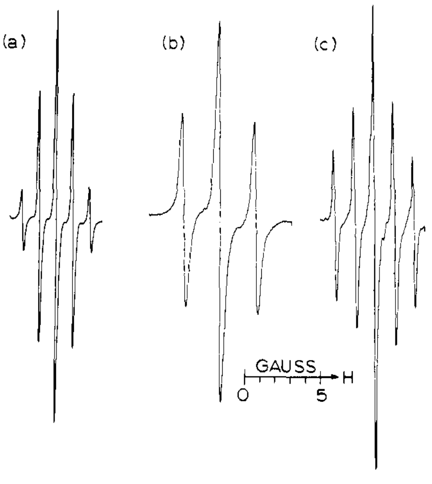

Figure 1. Radical anions derived from triptycene bis(quinone) in MeCN at 25 °C. (a) $1^{-}\cdot$, (b) $\cdot 1^{2-}\cdot$, and (c) $1^{3-}\cdot$ containing a trace of $\cdot 1^{2-}\cdot$ (shoulders on center and high-field peak).

In MeCN or Me_2SO **1** was reduced by KI in the presence of Hg or in MeCN by KI in the presence of [2.2.2]cryptand to give $\mathbf{1}^{-}\cdot$. The cryptand had no effect upon the spectra but only served to make KI a better reducing agent (without the cryptand and in the absence of Hg, the formation of radical anions from **1** and KI was not observed). As the amount of KI in the presence of Hg was increased, the initial pentet (Figure 1a) was slowly converted to the triplet (Figure 1b). Another reducing agent, potassium *tert*-butoxide, had the same effect in MeCN or Me_2SO.[6] Traces of *tert*-butoxide gave the 1:4:6:4:1 pentet, while larger amounts yielded the 1:2:1 triplet.

Radical Trianion of 1. More extensive electrolytic or chemical reduction of **1** led to a species with a lower g value than $\mathbf{1}^{-}\cdot$ or $\cdot\mathbf{1}^{2-}\cdot$. Continued electrolytic reduction at high voltages in Me_2SO or MeCN (Hg pool, $Bu_4N^+ClO_4^-$) produced a new pentet in addition to the composite spectra of Figure 1a and 1b. There was

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