Table I. Arrhenius Parameters for Quenching of Aromatic Hydrocarbon by 2,5-Dimethyl-2,4-hexadiene

Fluorescer (A*)	Electron affinity, eV[a]	$10^8 k_q$, M^{-1} sec^{-1} (23°C)[b]	$\Delta E^{\ddagger}$,[c] kcal	$\Delta S^{\ddagger}$, eu
Naphthalene	1.51	28	0.52	−16
		0.93[d]	−1.5[d]	
trans-Stilbene	1.37	160	3.3	−1
Anthracene	1.35	13	−2.8	
Fluoranthene	1.37	0.16	−7.4	
Triphenylene	1.24	0.15	1.5	−24
Phenanthrene	1.15	0.14	1.8	−22

[a] $-E_S - E_{1/2}(A/A^-)$, see text. [b] Obtained from the slope of linear Stern–Volmer plots for fluorescence intensity and/or lifetime quenching in degassed benzene solution. Singlet lifetimes measured by single-photon counting except for *trans*-stilbene ($\tau \sim 2 \times 10^{-10}$ sec[5b]). [c] Obtained from slope of plots of log (k_q) vs. T^{-1}, minimum of six temperatures between 5 and 75°C. Corrected for the variation in fluorescer singlet lifetime and solvent density with temperature. [d] Quenching by *cis*-1,3-pentadiene.

served fluorescence quenching rates (k_q) significantly slower than the rate of exciplex formation (eq 3, $k_p = k_n + k_r + k_a$). This report prompted us to examine the temperature

$$k_q = k_1(k_p)/(k_p + k_{-1}) \qquad (3)$$

dependence of the rate constants for quenching of aromatic hydrocarbon fluorescence by dienes.[14]

Arrhenius parameters for fluorescence quenching by 2,5-dimethyl-2,4-hexadiene are given in Table I. Values for *trans*-stilbene are consistent with diffusion-controlled, irreversible quenching.[13] Values of $\Delta E^{\ddagger}$ for all of the other aromatic hydrocarbons are smaller than 2 kcal/mol, negative temperature coefficients being observed for anthracene and fluoranthene. Negative temperature dependence is a consequence of a substantially more positive $\Delta S^{\ddagger}$ for exciplex dissociation (k_{-1}) than for exciplex reactions (k_p). Unfortunately, the individual rate constants in eq 3 cannot be separated due to the absence of exciplex emission.[13] However, it appears likely that the large variation in room temperature fluorescence quenching rate constants for *trans*-stilbene, anthracene, and fluoranthene (Figure 2) is the consequence of increasing exciplex reversibility rather than decreasing rates of exciplex formation.

Once the reversible nature of aromatic hydrocarbon-diene exciplex formation is recognized, the previously mentioned problems of interpreting exciplex kinetics can be readily explained. The decrease in fluorescence quenching rate constants with diene ionization potential (Figure 1) reflects increased reversibility of exciplex formation and not simply a decrease in the rate constant for exciplex formation.[2] Quenching of naphthalene by 2,5-dimethyl-2,4-hexadiene (IP = 7.84[1b]) displays a small positive temperature dependence, whereas quenching by *cis*-1,3-pentadiene (IP = 8.65[1b]) displays a negative temperature dependence. Reversible exciplex formation becomes increasingly important with less electron-rich dienes.[13] The absence of large kinetic solvent effects is also explicable in terms of reversible exciplex formation. Even if charge resonance stabilization is responsible for exciplex formation, no simple solvent dependence would be expected for the complex quenching rate constant (eq 3). Finally, the enhanced quenching of naphthalene and anthracene by cyclohexadiene vs. acyclic dienes[1b,c] may also be a consequence of reversible exciplex formation. Yang[6] has reported high quantum yields for 4 + 4 cycloadduct formation from naphthalene and anthracene with cyclohexadiene. If k_a (and hence k_p) is larger for cyclic vs. acyclic dienes with similar values of k_1 and k_{-1}, then enhanced quenching rates will be observed. Larger values of k_a would be expected for cyclic vs. acyclic dienes on the basis of increased frontier orbital overlap.[6b,7b,15] For *trans*-stilbene (Figure 1), triphenylene, and phenanthrene, frontier orbital overlap is comparable for cyclic and acyclic dienes, and enhanced quenching rate constants are not observed for cyclic dienes.

We conclude with a caveat concerning the interpretation of fluorescence quenching data obtained at a single temperature.[1-3,9] When quenching occurs via reversible exciplex formation, the observed quenching constants can be substantially lower than the rate constant for exciplex formation (eq 3). Changes in fluorescer and quencher structure can potentially alter all of the rate constants involved in exciplex formation and decay (eq 1).

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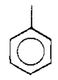
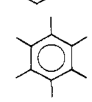
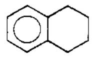
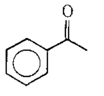
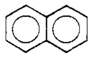
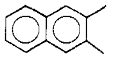
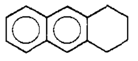
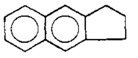
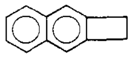
Electrochemical Generation of Stable Arene Metal Tricarbonyl Dianions

Sir:

Although a few reports have appeared in the literature regarding the nonaqueous electrochemical reduction of benzenetricarbonylchromium compounds, no detailed study has appeared regarding the reductive electrochemical characteristics of arene chromium carbonyl complexes.[1-4] Gubin has reported that the polarographic reduction of acetophenonetricarbonylchromium occurs by an electrode reversible one-electron process.[3,4] In contrast, Dessy et al.[1] report transferring two electrons per molecule of benzenetricarbonylchromium during an exhaustive controlled potential reduction. The resulting solution was oxidized to regenerate benzenetricarbonylchromium. In this paper, we wish to report our electrochemical studies on a variety of arene chromium carbonyl complexes in nonaqueous media and the

Table I. Pulse Polarographic Data for $ArCr(CO)_3$ and Anthraquinone (AQ)[a]

Compound	AR	$-E_{1/2}$, V	I_p	$E_{3/4} - E_{1/4}$	Solvent[b]
1		2.25	20.1	60	AN
2		2.50	18.8	60	AN
3		2.32	19.0	60	AN
4		1.59 1.59	3.5 *c*	60 60	PC AN
5		1.66 1.66	*c* 6.0	30 30	AN PC
6		1.72	5.9	30	PC
7		1.72	5.7	30	PC
8		1.75	*c*	30	PC
9		1.74	6.7	55	PC
AQ		0.94	3.1	60	PC
AQ		0.94	10.2	60	AN

[a] Potentials are referenced to the aqueous SCE. Supporting electrolyte is $(C_2H_5)_4NClO_4$. Solutions were about 10^{-3} in depolarizer. [b] AN is acetonitrile. PC is propylenecarbonate. Cyclics of complexes 4, 5, and 6 were done in both solvents. No significant changes were observed on changing solvents. Small potential changes were within experimental error. Complex decomposition was slower in PC, the preferred solvent for concentration sensitive measurements. [c] A partially decomposed sample prevented concentration sensitive measurements.

generation of a very stable arene-Cr(−II)-tricarbonyl dianion.

Using a PAR-174 polarographic analyzer, pulse polarograms were taken of the compounds in Table I. I_p, the polarographic constant for pulse polarography,[5] was measured for each complex and compared to the value measured for anthraquinone, a system known to undergo a reversible one-electron reduction in aprotic media.[6-8]

In every case except **4**, where measurements could be made, it was found that the π-arenetricarbonylchromium systems have constants twice that of anthraquinone. Assuming similar diffusion coefficients within the same solvent system,[9] all of the π-arenetricarbonylchromium systems except **4** undergo reduction by a simultaneous transfer of two electrons.

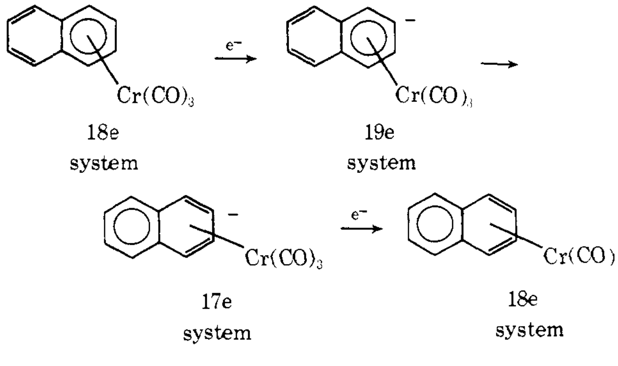
In order to substantiate our *n* values by a method insensitive to differences in diffusion coefficients, thin layer coulometry was carried out at a gold foil electrode according to the procedure developed by Murray et al.[10] We observed $n = 1$ for both anthraquinone and complex **4**, and $n = 2$ for **6**. The solution breakdown potential on the gold electrode was not sufficiently cathodic to allow a thin layer reduction of the benzene complex series, **1** through **3**. Nevertheless, our data do substantiate the assumption that diffusion coefficient differences in these molecules are small. Coulometry at a mercury pool electrode on **1** also yielded $n = 2$.

Gubin[3] has suggested the one-electron reduction of **4** involves radical anion formation, the odd electron being localized primarily on the organic ligand. We have found that cyclic voltamograms of **4** in acetonitrile, THF, and DMSO are chemically irreversible ($i_p(\text{anodic})/i_p(\text{cathodic}) = 0$) indicating very rapid decay of the radical anion. Spectroscopic observation of the radical anion then was not possible, and we are unable to confirm Gubin's speculation. It is clear, however, that the presence of a carbonyl on the organic ligand sufficiently perterbs the system to alter the fundamental nature of the electrochemical reduction. A second wave at −2.4 V is observed. However, the chemical irreversibility of the system precludes meaningful speculation about the nature of the species formed.

The benzenetricarbonylchromium systems, **1** through **3**, differ from the naphthalenetricarbonylchromium systems, **5** through **8**, in electrode reversibility. On a polarographic time scale, the naphthalene complexes are reversible, with a polarographic slope of 30 mV. The 60 mV slope of the benzene systems, **1** through **3**, suggest an irreversible reduction. The naphtho[*b*]cyclobutene complex, **9**, is an anomaly which will be discussed, vide infra. Cyclic voltammetry and exhaustive controlled potential electrolysis were used to further detail the difference between the benzene and the naphthalene compex series.

The cyclics of the benzene series show only a small anodic wave in the region of the cathodic peak for sweep rates above 10 V/sec. In contrast, the naphthalene systems, **5** through **8** in Table I, all had clearly defined anodic peaks in a one to one current ratio with the cathodic peaks for sweep rates as low as 0.05 V/sec. Furthermore, for sweep rates below 0.1 V/sec the cathodic and anodic peak potentials were separated by 30 mV, further substantiating a two-electron reversible mechanism. However, as the sweep rate increased, the peak separation increased. Such an increase was not observed for the reversible anthraquinone system, suggesting that the naphthalene system is pseudo-reversible on the time scale of cyclic voltammetry.

Our data suggest, then, that the naphthalene systems are reduced by a pseudo-reversible, two-electron transfer to form a dianion intermediate.[16] In aprotic solvents, multielectron reductions are typically associated with rapid following chemical kinetics such as decomposition or proton abstraction. The observation of a two-electron reduction to a stable dianion species is therefore unusual.[11] It has been suggested that such a two-electron process is probably best described as the transfer of one electron followed stepwise by the second electron at an E^0 potential anodic to the first.[12,13] On qualitative theoretical grounds Bard[12] points out that if the E^0 of the second electron transfer is anodic to the first, an ECE type mechanism must be invoked. The nature of the interim "chemical" step may involve solvent reorganization, geometric isomerization, or some other reversible, fast equilibrium at the outer Helmholz plane. We would like to suggest that the interim chemical step involves the geometric isomerization shown below. The 18-electron chromium(0) complex upon reduction would give an unstable 19-electron system. The molecule can relieve this situation by having the $Cr(CO)_3$ group move slightly and bond



just to the butadiene moiety. This radical anion is now only a 17-electron system and would be expected to be readily reduced to the 18-electron dianion.[16]

Exhaustive controlled potential electrolysis on a mercury pool electrode of toluenechromium tricarbonyl, **1**, in THF results in a solution which shows an ill-defined oxidative polarographic wave in the region of −0.5 V. Oxidation of this solution regenerates the polarographic wave for **1**, in agreement with the work of Dessy.[1] Furthermore, electrolysis of a propylenecarbonate solution of either of the naphthalene complexes, **5** or **6**, results in a solution with an oxidative polarographic wave in the region of −0.5 V. Oxidation of this solution also regenerates the polarographic wave of the initial complex.

However, in a THF solution (freshly distilled from $LiAlH_4$) exhaustive electrolysis of **5** or **6** results in an oxidative wave only 150 mV anodic to the wave for the initial complex. Oxidation at a potential on top of the oxidative wave regenerates the wave for the initial complex. Ir and uv analysis confirms the regeneration of the complex. Furthermore, cyclic voltammograms of **5** or **6** in THF solution show the cathodic and anodic peaks separated by 150 mV, with much adsorption in the anodic cycle. Also, the polarograms of **5** and **6** in THF have slopes of about 45 mV These data are consistent with the formation of a dianion species by a pseudo-reversible, two-electron process under conditions in which the dianion is stable.[16]

Generation of the dianion solution electrochemically, followed by protonation with either water or benzoic acid (in excess of 2 equiv), generated a solution with an oxidative polarographic wave in the region of −0.5 V. This solution can be reoxidized electrochemically at −0.4 V to generate the wave for the unreduced complex.

The difference between the benzene series, **1** through **3**, and the naphthalene series, **5** through **8**, then is one of degree, and not kind. Both systems undergo a two-electron reduction. The benzene system reduces irreversibly with rapid follow up chemical kinetics. The naphthalene system reduces pseudo-reversibly with relatively slow follow up chemical kinetics, presumably protonation. The products of the follow up chemical kinetics in either case, however, may be oxidized to the original complex.

Compounds **6** through **9** are capable of existing in two different isomers. In fact, NMR on the starting samples indicated that complexes **6**, **8**, and **9** were mixtures of two isomers.[15] Deubzer[14] has shown that in compound **6** the equilibration of the isomers is negligibly slow at ambient temperatures. However, differential pulse polarographic analysis of **6** and **8** showed only one peak. This would suggest that the lowest unoccupied orbital into which the extra electrons are going is predominantly centered on the $-Cr(CO)_3$ group. Two peaks were observed, however, for **9**. Computer simulation of the current-voltage curves indicated that the two peaks resulted from each isomer undergoing a two-electron reduction with a separation of $E_{1/2}$ values of 40 mV. The computer simulation ruled out the possibility that the two peaks simply represented the first and second reduction potential with both isomers having the same first and second reduction potentials.

The possibility existed that the identical reduction potentials of the isomers of **6** and **8** might arise by some fluxional behavior. The two isomers of 2,3-dimethylnaphthalenechromium tricarbonyl were separated by fractional sublimation. The isomeric purity of each isomer was examined by high speed liquid chromatography. Exhaustive controlled potential electrolysis of either of the isomers in THF, followed by reoxidation, resulted in recovery of only the initial isomer. Analysis of products was by liquid chromatographic retention times, and by uv and ir spectroscopy. In the dianion, then, the chromium atom is associated with only one ring of the naphthalene system, as in the unreduced complex.

We are continuing to examine the generality of the reduction of chromium and other metal arenecarbonyl complexes. This along with ac-polarographic and chemical reduction data will be reported in the near future.

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Carbon-13 CIDNP during the Photolytic Decomposition of *tert*-Butyl Hydroperoxide in 2-Propanol. Detection of Transient Intermediates

Sir:

We report the observation of carbon-13 CIDNP signals from keto-enol tautomers and a hemiketal formed during photolysis of *t*-BuOOH in 2-propanol. Direct evidence for these species as well as an insight into the mechanism of their formation was obtained.

Photolysis of 10-50% solutions of *t*-BuOOH in 2-propanol was performed inside the modified probe of a Varian HA-100 pulsed carbon-13 NMR spectrometer. The irradiation from a 600-W mercury-xenon arc source was focused through a water filter and onto the polished end of a quartz rod which terminated 1 mm from the bottom of the Pyrex sample tube. Figure 1A shows a typical carbon-13 proton