Table I. Calculated $C(p_z)$ Wave Function Coefficients for N···B at $r = 5$ Å and $r = 2.90$ Å[a]

atom[b]	coefficient for MO[c,d]			
	34	35	36	37
	r = 5 Å			
C_1	+0.465	0	+0.397	0
C_2	−0.308	0	+0.269	0
C_9	+0.005	0	−0.010	0
C_{13}	0	−0.434	0	−0.339
C_{14}	0	+0.654	0	−0.573
	r = 2.9 Å			
C_1	+0.256	−0.359	+0.368	+0.152
C_2	−0.203	+0.227	+0.230	+0.148
C_9	+0.095	−0.047	−0.047	−0.111
C_{13}	−0.305	−0.277	+0.225	−0.254
C_{14}	+0.469	+0.429	+0.370	−0.417

[a] $d = 2.51$ Å. [b] See **1** for numbering. [c] See note 12; MO 34 is N-localized LUMO, 35 is B LUMO, 36 is N HOMO, 37 is B HOMO at $r = \infty$. [d] Symmetry designations within local C_s point group are 34 (a′), 35 (a′), 36 (a″), 37 (a″).

occurs with the next highest (bound) state E_3. Since the two state symmetries are the same (A''), an avoided crossing will result, allowing access to the second minimum at $r = 3.16$ Å ($d = 2.51$ Å). At the second minimum, and in the region 4 Å $> r > 3.16$ Å, the states E_1 and E_2 are calculated to lie within 0.02–0.04 eV of one another. We therefore anticipate rapid interconversion among the upper states E_2 and E_1 in the interaction region. This path provides a plausible mechanism for the quenching of N* by B^0, since, once access has been gained to the E_1 minimum, rapid radiationless decay of the exciplex is to be expected by virtue of electronic mixing of the short-lived butadiene localized excited state into the longer-lived naphthalene localized state.

We note that the calculations reported here strictly apply only to the exciplex state uninfluenced by solvent. In fluid media, overall exciplex decay processes are dependent on factors which involve solvent, e.g., ion-pair separation. Mixing of ionic (CT) and excitation resonance configurations results in a positive binding energy for the exciplex state. In a polar solvent, exciplex binding energy is lower than in nonpolar solvents since ion-pair separation is increased. We suggest that the present calculations present an accurate picture of the configurationally mixed exciplex state in nonpolar solvents, and that the minimal contribution of CT stabilized configurations (7%) to the total exciplex state at the minimum is an important result which demands experimental study.

We believe that the EHT procedure provides an attractive framework for examination of the electronic nature of exciplex interactions in model systems which closely resemble actual experimental ensembles. We are extending this study to other systems[13] and to the use of other relatively simple and accessible molecular orbital techniques.

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(10) These programs are part of the TRIBBLE system, an interactive "computational workbench," specifically designed to make the computer easily accessible to laboratory chemists: D. Pensak, in preparation.
(11) EHT places the localized HOMO's and LUMO's of N and B in the following energy order: LUMO (N) > LUMO (B) ≫ HOMO (N) > HOMO (B), with E (LUMO–HOMO)$_N$ < E (LUMO–HOMO)$_B$. Thus, the lowest energy excited state is formally N⁺···B⁻, followed by N⁰···B⁰, N⁰···B*, and N⁻···B⁺, respectively, at infinite separation. More sophisticated calculations place LUMO (B) above LUMO (N) and eliminate this anomaly, which does not affect the present results in substance.
(12) The N···B supermolecule is a system of 140 electrons, 70 MO's. Virtual orbitals are numbered 1–35, inclusive, while MO's 36–70 are doubly occupied in the ground configuration. MO 34 is associated, at large *r*, with the N-localized LUMO; likewise, MO 35 is LUMO (B), MO 36 HOMO (N), MO 37 HOMO (B). All the above are π-like $C(p_z)$ ao combinations.
(13) Calculations in progress include N···B exciplexes with s-trans diene; the effect of geometry relaxations (e.g., H bending) near the minimum; and the naphthalene–quadricyclane exciplex.

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Electrochemical Properties of Bis(cyclopentadienylcobalt)cyclooctatetraene. Formation of a 34-Electron Triple-Decker Compound

Sir:

We report the electrochemical generation of the dication of bis(η^5-cyclopentadienylcobalt)cyclooctatetraene, $(CpCo)_2COT^{2+}$, a formal member of the so-called "triple-decker sandwich" class of molecules. This complex contains 34 valence electrons and is isoelectronic with the tris(cyclopentadienyl)dinickel cation (**1**), the only charged triple-decker to be previously reported.[1-3]
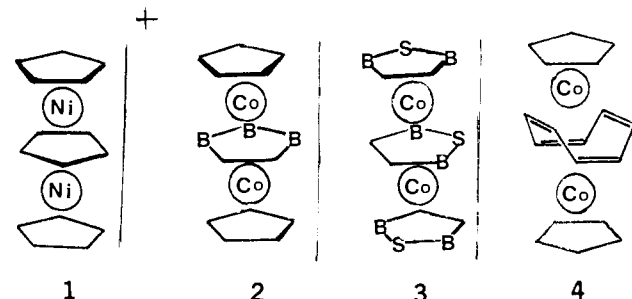
Triple-decker complexes of the type **1–3** represent an intriguing class of organometallic compounds which has only recently been discovered.[1-9] All of the reported compounds contain either 30 or 34 valence electrons, a characteristic accounted for by the theoretical treatment of Hoffmann and co-workers.[10]

$(CpCo)_2COT$ (**4**) has 18 valence electrons around each metal for a total of 36 electrons, and has been categorized as a "near miss" to the triple-decker class.[10] As part of our investigation of the redox properties of triple-decker sandwiches
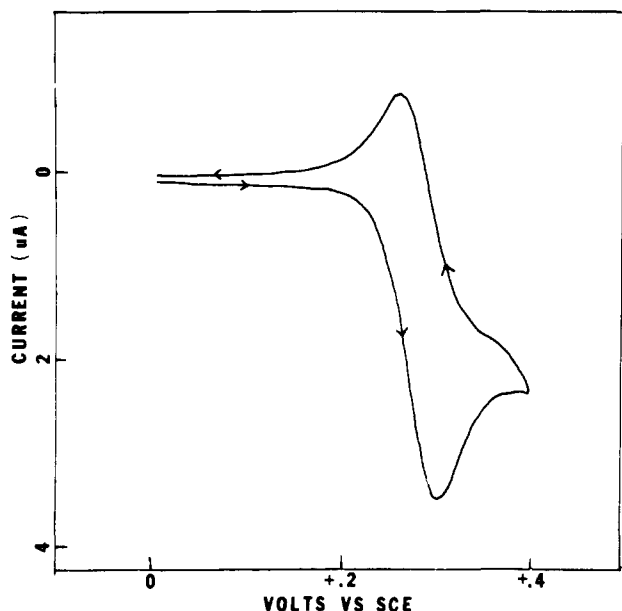
Figure 1. Cyclic Voltammogram of $(CpCo)_2COT$ in $CH_2Cl_2/0.1$ M Bu_4NPF_6 at a hanging mercury drop electrode: scan rate, 50 mV/s.

and other multimetallic compounds, we were interested in the possibility that **4** could be oxidized by two electrons to give a $34\text{-}e^-$ triple-decker compound.

The oxidation of this compound in nonaqueous electrolytes is very facile. A polarographic $E_{1/2}$ of ca. +0.1 V was found for dichloromethane solutions containing 0.1 M Bu_4NPF_6 supporting electrolyte. In CH_2Cl_2, the oxidation is a *reversible, two-electron* process. The shape of the polarographic wave supports this conclusion, for a plot of $-E$ vs. log $[i/(i_d - i)]$ is linear with a slope of 35 mV (theory: 29.5 mV for a reversible $2\text{-}e^-$ change, 59 mV for 1 e^-). For cyclic voltammetry (CV) measurements, at either mercury or platinum electrodes, a luggin probe[12] and positive feedback iR compensation were employed in order to minimize the resistance effects commonly found when using dichloromethane electrolyte solutions. CV peak separation as low as 32 mV (scan rate, 24 mV/s) were found. A typical CV scan is given in Figure 1. The dication is highly reactive and is subject to a follow-up reaction subsequent to the reversible, two-electron, oxidation. The measured values of i_c/i_a establish this, for scan rates in excess of 100 mV/s were necessary to reach the value of 1.0 (0.85 at 60 mV/s) expected for a completely stable electrolysis product.[13] The reactivity of the dication is discussed further below.

Bulk anodic oxidation confirmed that 2 electrons are released. Our attempts to isolate a pure sample of the dication have been unsuccessful to this point. Brown solids can be isolated from solutions of **4** oxidized by either anodic or chemical $(AgPF_6)$ means, but recrystallization has resulted in decomposition, due to the high susceptibility of the dication to nucleophilic attack.
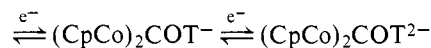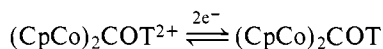
In this regard, the chemistry of $(CpCo)_2COT^{2+}$ is very similar to that of $Cp_3Ni_2^{+}$.[1-3] Generation of the dication in a basic solvent such as CH_3CN results in its instant decomposition. CV measurements in CH_3CN/Bu_4NPF_6 demonstrate this most effectively. The oxidation of **4** is completely irreversible in this solvent, with additional waves appearing at e_{p_a} = +0.26 and +1.57 V in the scan. These waves are due to the oxidation of $CpCo(COT)$,[14] which we are studying independently. This species most likely arises through the reaction

$$(CpCo)_2COT \rightleftharpoons (CpCo)_2COT^{2+}$$

$$+ 2e^- \xrightarrow{CH_3CN} CpCoCOT + CpCo(NCCH_3)_n{}^{2+}$$
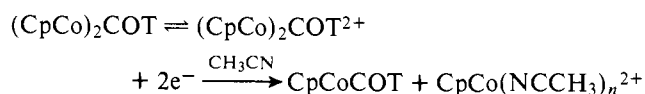
Something can be said about the electron-transfer mechanism $(CpCo)_2COT^{0/2+}$. The two electrons must be transfered one at a time, and a separate $E^°$ value can be assigned to each electron transfer. The potential of the 2nd electron transfer, $E_2^°$, must be less than or equal to that of the first transfer, $E_1^°$, in order for the overall process to involve 2 electrons without observation of a 1-electron intermediate. CV peak separations of 42 or 60 mV are expected for cases in which $E_2^° = E_1^°$, depending on whether or not there is strict electronic isolation of the redox sites.[15-17] A peak separation of 30 mV is expected for the $E_2^° < E_1^°$ case, and our observed value of 32 mV means that this situation describes the oxidation of **4**.

There is other, supporting, evidence that the 2-electron process does not occur because of simultaneous oxidation of 2 noninteracting cobalts. The *reduction* of this molecule (in CH_3CN or THF) occurs in two *1-electron* steps ($E_{1/2} = -2.23$ and -2.70 V), the first of which is highly reversible by the usual[18] standards (in CH_3CN, $\Delta e_p = 60$ mV, $i_{p_a}/i_{p_c} = 1.0$ at all scan rates, $i_p/V^{1/2}$ constant). The observation of discrete 1-electron, rather than 2-electron, reductions supports the fact that there is electron interaction between cobalt atoms. Finally, unpublished extended Hückel calculations performed on the neutral molecule by Hoffmann conclude that both the lowest unoccupied and highest occupied molecular orbitals are delocalized over the metals and ligands.[19] The 2-electron oxidation can then be seen to involve a significant gain in stabilization energy for the dication, compared with that of a hypothetical monocation. This might involve unusually favorable solvation of the dication, or a gain in resonance energy from, for example, flattening of the COT ring. We are continuing efforts to isolate the dication in hopes of shedding light on the question of its structure.

Thus, **4** undergoes a set of electron-transfer reactions as shown:

$$(CpCo)_2COT^{2+} \underset{}{\overset{2e^-}{\rightleftharpoons}} (CpCo)_2COT$$

$$\overset{e^-}{\rightleftharpoons} (CpCo)_2COT^- \overset{e^-}{\rightleftharpoons} (CpCo)_2COT^{2-}$$

It is possible that other triple-decker complexes may be accessible by electrochemical oxidation or reduction of multimetallic π compounds.[20] Studies of electron-transfer reactions of these complexes should be informative about the nature of the metal–metal interactions in delocalized species. We will report more extensive data on the above compounds and on triple-decker complexes like **2** in subsequent communications.

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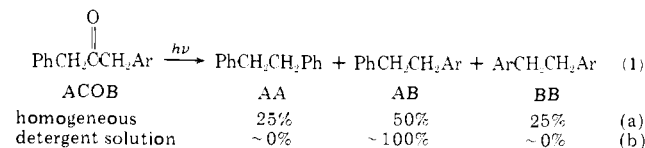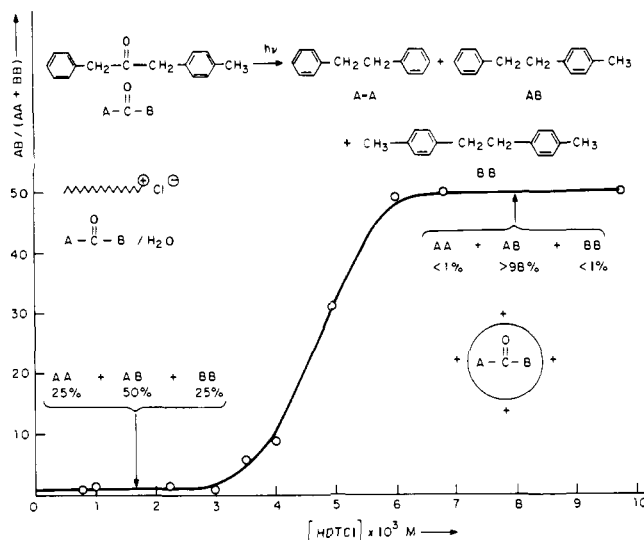Burlington, Vermont 05401*

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Figure 1. Variation on the ratio of the asymmetric coupling product (AB) to the (sum of the) symmetric coupling products (AA + BB) as a function of detergent concentration. The ketone concentration was fixed at 4×10^{-4} M.

Photoreactions in Detergent Solutions. Enhancement of Regioselectivity Resulting from the Reduced Dimensionality of Substrates Sequestered in a Micelle

Sir:

Below the critical micelle concentration (cmc), detergents exist mainly as monomers in aqueous solution,[1] whereas at higher concentration (above the cmc) these amphiphiles aggregate to form globular micelles that are characterized by a hydrocarbon-like interior ("inside"), a hydrophilic, highly polar and ionic surface ("boundary"), and an aqueous exterior ("outside"). For example, the conventional model[2] of hexadecyltrimethylammonium chloride (HDTCl) indicates that above the cmc this detergent becomes organized to form (roughly spherical) micelles consisting of 50–70 monomers. Micelles can be employed to organize organic substrates in detergent solutions. The influence of organizational aspects of micelles has provide information on numerous micellar catalyses,[3] photophysical[4] and photochemical[5,6] processes. It is also possible to reverse the strategy and use photophysical and photochemical information to deduce the structural and dynamic properties of micelles. We report here a study of the influence of micelle formation on the selectivity of a photoreaction. Our results provide information on the dynamics of organic solutes in micellar systems and indicate a means of enhancing reaction selectivity by taking advantage of the "reduction of dimensionality" enforced upon hydrophobic reagents that are sequestered into a micellar environment.

The photodecarbonylation of dibenzyl ketones in homogeneous fluid solution occurs via a free-radical mechanism in which coupling products (1,2-diarylethanes) are produced in quantitative yield.[7] For an asymmetric dibenzyl ketone (ACOB) the coupling products AA, AB, and BB are formed in yields of 25, 50, and 25%, precisely the ratio expected for statistical, nonselective coupling of the free radicals $\dot{A}$ and $\dot{B}$ produced by photodecarbonylation (eq 1a).

$$\underset{\text{ACOB}}{PhCH_2\overset{\overset{\displaystyle O}{\|}}{C}CH_2Ar} \xrightarrow{h\nu} \underset{\text{AA}}{PhCH_2CH_2Ph} + \underset{\text{AB}}{PhCH_2CH_2Ar} + \underset{\text{BB}}{ArCH_2CH_2Ar} \quad (1)$$

	AA	AB	BB	
homogeneous	25%	50%	25%	(a)
detergent solution	~0%	~100%	~0%	(b)

Irradiation of (p-tolyl)benzyl ketone (ACOB) in benzene,[7] or in water,[8] yields a statistical mixture of coupling products (eq 1, Ar = p-CH₃C₆H₄). Addition of HDTCl to aqueous solutions of ACOB causes a remarkable effect on the product mixture (Table I).[9] The yield of AB relative to AA + BB is a dramatic function of added HDTCl (Figure 1). Since the ratio of AB/(AA + BB) shows marked increases only above a concentration of HDTCl that is 10^{-3} M (the reported cmc of

Table 1. Ratio of AB/[AA + BB] as a Function of Ketone and Detergent Concentration

[HDTCl][a]	[ACOB][b]	ketone/micelle[c]	AB/[AA + BB]
1×10^{-3}	4.4×10^{-4}	44	1.4
5×10^{-3}	4.4×10^{-4}	9	6.7
1×10^{-2}	4.4×10^{-4}	4	~50
2.5×10^{-2}	1.6×10^{-4}	0.6	~50
2.5×10^{-2}	5.8×10^{-4}	2.4	3.8
2.5×10^{-2}	1.2×10^{-3}	4.8	2.5
2.5×10^{-2}	7.4×10^{-4}	2.9	3.2
2.5×10^{-2}	7.4×10^{-4}	2.9	~50[d]

[a] Hexadecyltrimethylammonium chloride. [b] (p-tolyl)benzyl ketone. [c] The mean number of ketone molecules per micelle, calculated on the assumption that the aggregation number of HDTCL = 100. [d] Solutions contain 0.01 M CuSO₄.

this detergent),[10] we conclude that the selectivity is micellar in origin. Above the cmc, the quantum yield for reaction in detergent solution is $\sim^1/_3$ for that in benzene solution.

By controlling the ratio of ketone to detergent (above the cmc), situations may be created so that micelles contain zero, one, or more ketone molecules.[11] Photolysis leads to generation of $\dot{A}$ + $\dot{B}$ within a single micelle.[13] In homogeneous solution $\dot{A}$ and $\dot{B}$ diffuse apart to become "free" radicals, but, when they are both produced in a single micelle, they are sequestered in a special environmental "cage" (Figure 2). Since $\dot{A}$ and $\dot{B}$ are hydrophobic they are effectively confined to the "reduced dimension" of space defined by the hydrophobic portion of the micelle, i.e., its "inside". In order for products of the type AA or BB to form, two $\dot{A}$ or two $\dot{B}$ radicals must diffuse together. Several mechanisms for formation of AA and BB are therefore possible. For example, $\dot{A}$ and $\dot{B}$ may diffuse out of their original "cage", and enter the aqueous phase. Formation of AA and BB may occur by reaction of radicals in the aqueous phase or by penetration by $\dot{A}$ or $\dot{B}$ of the boundary of a micelle containing a radical of the same type. Collisions between micelles also provide a mechanism for generation of AA and BB, but such a mechanism is unlikely to be effective since the common exterior charge causes repulsion between micelles and in addition only collisions between micelles both of which happen to contain $\dot{A}$ and $\dot{B}$ can cause the scrambling.[15]

The occurrence of two or more ketones in a single micelle would enhance the formation of AA and BB, only if two $\dot{A}$ (or