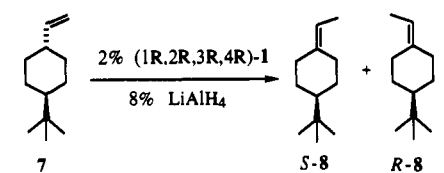


Table I. Asymmetric Alkene Migration Catalyzed by 1^a


entry	temp (°C)	time (h)	yield	% ee ^b of (S)-8
1	180	2	100	44
2	180	12	100	14
3	80	12	100	65
4	80	24	100	55
5	50	17	100	74 ^c
6	23	120	100	76
7	23	67	24 ^d	80

^a Reaction procedure: (1R,2R,4R,5R)-1 (5.1 mg, 0.010 mmol) and LiAlH₄ (Fluka 97%, 1.6 mg, 0.04 mmol) in mesitylene (0.3 mL) were heated in an ampule at 164 °C for 30 min and then cooled to 23 °C. *trans*-7 in *n*-decane as internal standard (0.2 mL, 0.5 mmol) was added and the sealed ampule heated at the indicated temperature for the indicated time. ^b Determined by chiral gas chromatography (50 m CP-cyclodex β-236, 80 °C isothermal, 15 psi, R_f (R)-8 77.02 min, (S)-8 77.74 min). ^c [α]_D²⁵ +11.5° (c 3.01, 27:1 mesitylene/decane) indicates formation of the *S* isomer, ref 11. ^d *trans*-7 recovered in 76% yield.

in the bridging group, we convert the previously enantiotopic faces of the indenyl ligands into diastereotopic faces and can theoretically favor the formation of a single stereoisomer of a single diastereomeric bis(indenyl)metal complex, eliminating the need for separating and resolving the complex.

The facile preparation of bis(indenyl)titanium complex 1 from the known (1*S*,2*R*,4*S*,5*R*)-2,5-diisopropylcyclohexane-1,4-diol (3)⁷ is shown in Scheme I. Addition of indenyllithium to the bis-(methanesulfonate) ester of diol 3 yielded either the spiroannulated indene 5 or the desired bis(indene) 4, depending on the reaction conditions. Addition of indenyllithium in THF to the dimesylate of 3 in the presence of HMPA gave almost exclusively the spiro product 5, which could be thermally converted^{7,9} to the novel fused indene 6. Carrying out the displacement in Et₂O gave a 60% yield of the desired C₂-symmetric bis(indene) (1*R*,2*R*,4*R*,5*R*)-4 as a mixture of double-bond isomers. Addition of the *n*-butyllithium-generated dianion of bis(indene) 4 to TiCl₃ followed by oxidation with HCl/air in CHCl₃ gave an 80% yield of a single isomer of *ansa*-bis(indenyl)titanium dichloride 1. The solid-state structure of this complex was determined by X-ray diffraction of a suitable single crystal and is shown in Figure 1.⁸ We rationalize the very high yield of a single isomer of metallocene 1 as being due to the highly preferred placement of the indenyl moieties away from the isopropyl groups on the bridging cyclohexane ring.

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The catalytic isomerization of achiral alkenes using prerduced achiral titanocene dichlorides has been developed previously and is postulated to occur via an (η¹-allyl)- or (η³-allyl)titanium hydride intermediate.¹⁰ In order to study an asymmetric version of this isomerization, we chose to examine the conversion of the achiral meso *trans*-4-*tert*-butyl-1-vinylcyclohexane (7), a molecule devoid of any functionality other than the single vinyl group, into the chiral axially dissymmetric ethylenecyclohexane 8. In our case, we reduced our precatalyst, *ansa*-bis(indenyl)titanium dichloride (1*R*,2*R*,4*R*,5*R*)-1, with LiAlH₄ and then introduced 50 equiv of *trans*-7 at various temperatures. As shown in Table I, the chiral alkene product (S)-8 was formed in up to 80% enantiomeric excess in generally quantitative yield. The rate of the reaction and the enantiomeric purity of the product are strongly dependent on the reaction temperature. The lower enantiomeric purity obtained at the higher temperatures is apparently due to racemization by equilibration of the product, a process which should be enhanced with longer reaction times (as evident from entries 1–4). Isolated, enantiomerically enriched 8 was resubjected to the reaction conditions at 50 °C, affording a slightly diminished enantiomeric purity of 8 (74 to 71% ee after 24 h), which indicates probable slow equilibration of the ethylenecyclohexane at this lower temperature. Further studies on the origin of enantioselectivity, the scope, and the mechanism of this unique asymmetric isomerization of an unfunctionalized alkene are in progress.

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Supplementary Material Available: Tables of bond lengths and angles, crystallographic data, and thermal and positional parameters for 1 (12 pages); listings of *h*, *k*, *l*, *F*_o, *F*_c, and σ(*F*_o) for 1 (17 pages). Ordering information is given on any current masthead page.

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Electron Transfer to Triplet C₆₀

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The recent isolation of fullerenes such as C₆₀ and C₇₀ has led to several studies of the reactivity and physical properties of their excited states.^{1–10} We recently reported that triplet C₆₀ (³C₆₀)

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Table I. Half-Peak Oxidation Potentials ($E_{1/2}(\text{ox})$), Calculated Energies for Electron Transfer (ΔG_{et}), and ${}^3\text{C}_{60}$ Quenching Rates (k_{q}) of Electron Donors

quenching donor	$E_{1/2}(\text{ox})^a$ V vs SCE	ΔG_{et}^b kcal/mol	k_{q}^c $10^9 \text{ M}^{-1} \text{ s}^{-1}$
tetramethylphenylenediamine	0.14 ^d	-22.9	5.2
<i>p</i> -anisidine	0.56 ^{e,f}	-13.3	5.1
<i>N,N</i> -diethylaniline	0.64 ^{e,f}	-11.4	2.6
<i>N,N</i> -dimethylaniline	0.71 ^g	-9.8	3.2
diphenylamine	0.84 ^g	-6.9	0.87
triphenylamine	0.85 ^g	-6.7	0.89
tripropylamine	0.94 ^{h,f}	-4.5	0.94
triethylamine	0.96 ^{h,f}	-4.0	0.96
aniline	0.98 ^d	-3.6	0.22
dipentylamine	1.16 ^{h,f}	0.6	0.076
dibutylamine	1.17 ^{h,f}	0.8	0.072
pyrrole	1.20 ⁱ	0.7	0.000091
dipropylamine	1.23 ^{h,f}	2.2	0.065
diethylamine	1.31 ^{h,f}	4.0	0.042
dibenzylamine	1.36 ^{h,f}	5.2	0.13
pyrene	1.36 ^{h,f}	5.2	0.00074
pyridine	2.12 ^{k,f}	22.7	0.00076

^a CH₃CN, room temperature. ^b $\Delta G_{\text{et}} = 23.06[E_{1/2}(\text{ox}) - (-0.51) - 1.56 - 0.085]$, see refs 34 and 35. ^c Average of values at 740 and 680 nm, except where radical cation spectra interfered at 680 nm (diphenylamine, triphenylamine, and aniline). ^d Reference 38, vs SCE. ^e Reference 39, vs Ag/Ag⁺. ^f Converted to SCE by adding 0.30 V according to values in refs 40 and 41. ^g Reference 42, vs SCE. ^h Reference 43, vs Ag/Ag⁺ (*Encyclopedia of Electrochemistry*⁴⁴). ⁱ Reference 45, vs SCE. ^j Reference 40, vs Ag/Ag⁺. ^k Reference 41, vs Ag/Ag⁺.

is formed with a quantum yield of 1.0¹¹ and has an energy near 35 kcal/mol; these values have since been confirmed.^{3,5,8,10} Recent photothermal determinations of the triplet energy are close to 36 kcal/mol.^{3,10}

Electrochemical studies have shown that C₆₀ is easily reduced ($E_1 = -0.33$ V vs Ag/AgCl in benzonitrile¹² and -0.42 V vs SCE in benzonitrile^{13,14}). The reduction potential of ${}^3\text{C}_{60}$ should be higher than that of the ground state by the amount of the triplet energy,¹⁵⁻¹⁸ 1.56 V. Recently, Verhoeven et al.¹⁹ observed reduction of an excited state of C₇₀, which has properties similar to those of C₆₀.²

Saturated ($2-5 \times 10^{-4}$ M) solutions of C₆₀ and added donor in benzonitrile under argon were studied by laser flash photolysis.²⁰ The quenching rate constants of triplet ${}^3\text{C}_{60}$ by electron donors (amines and pyrene) were determined from the decay kinetics of transient ${}^3\text{C}_{60}$ triplet-triplet absorption at 740 and 680 nm^{2,6-8} following excitation at 532 nm. In each case, the quenching followed eq 1:

$$k_{\text{obsd}} = k_{\text{d}} + k_{\text{q}}[\text{Q}] \quad (1)$$

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(20) The apparatus has been described previously.²

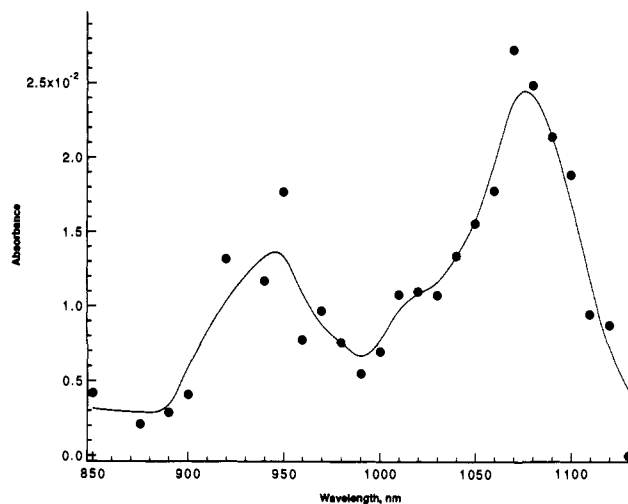


Figure 1. Transient absorption spectrum of C₆₀ radical anion, generated by laser photolysis at 532 nm of an argon-purged sample of C₆₀ ($\sim 5 \times 10^{-4}$ M) and *N,N*-dimethylaniline (0.019 M) in benzonitrile. The solid line is a smoothed curve through the points.

where k_{obsd} is the observed first-order decay rate constant of the triplet, k_{d} is the rate constant without quencher, [Q] is the concentration of the donor, and k_{q} is its bimolecular quenching rate constant. Plots of k_{obsd} vs [Q] (minimum of three concentrations) gave straight lines with correlation coefficients ≥ 0.98 .²¹ The quenching rate constants (k_{q}) are listed in Table I.

Quenching of ${}^3\text{C}_{60}$ occurs primarily by electron transfer, as shown by the formation of absorbing transients (350-800 nm) of aromatic amine radical cations. For example, the transient absorption spectrum from C₆₀ + *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) has maxima at 560 and 610 nm, in good agreement with previous reports of the TMPD radical cation spectrum.^{22,23} Other radical cation spectra were also similar to those reported: diphenylamine, 680 nm;²³⁻²⁶ triphenylamine, broad maxima at 550 and 650 nm;²³ *N,N*-diethylaniline, 480 and 710 nm;^{23,27} *N,N*-dimethylaniline, 450 and 470 nm;²³ and aniline, 440 and 740 nm.²³ In pulsed solutions of C₆₀ with excess triethyl- or tripropylamine (0.0072 M), where ${}^3\text{C}_{60}$ was >99.5% quenched, no transient absorption was produced.

No transient absorption assignable to C₆₀ radical anion was observed in the visible region. Two recent papers have reported that this species has weak absorbance at approximately 420 nm.^{28,29} However, the triplet has significant absorption in this region as do many of the amine radical cations. In studies using an infrared-sensitive germanium detector (North Coast EO817P), a transient with maxima at 950 and 1075 nm was observed (Figure 1), in good agreement with previous measurements of the transient infrared absorption of C₆₀ radical anion.^{9,28,30,31} The spectrum

(21) Benzonitrile (Eastman) and triethylamine (Fisher) were purified by washing with K₂CO₃, followed by distillation from P₂O₅; triphenylamine (Eastman) was recrystallized from methanol; and *N,N*-diethylaniline (Aldrich) was vacuum-distilled. Pyrene (MC&B), aniline (Fisher), pyridine (Mallinckrodt Spectranalyzed), and other amines (Aldrich) were used as received. C₆₀ was prepared and purified by the previously reported method.⁴⁹ Solutions of C₆₀ and the donor ($A_{532} = 0.16-0.32$) were excited by a Quanta-Ray DCR-2 Nd:YAG laser (3-6 mJ/pulse) at 532 nm. Transient signals were detected and analyzed by the method reported previously.²

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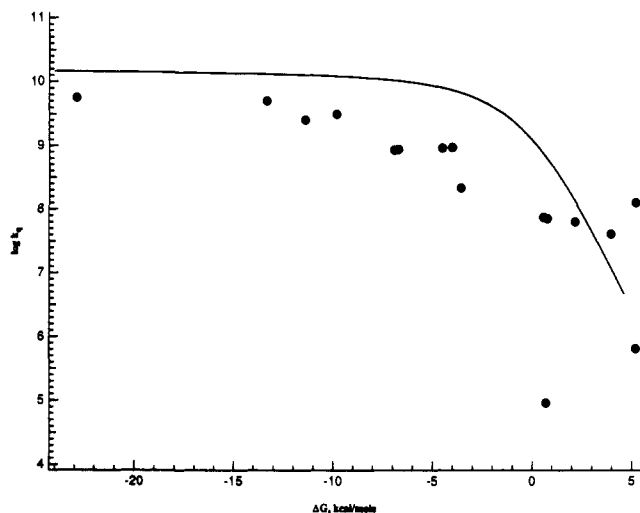


Figure 2. Plot of $\log k_q$ vs ΔG_{et} , see Table I and text. The solid line was calculated from the equation of Rehm and Weller.¹⁸

agrees well with that observed by Sension et al.,²⁸ who also reported photochemical reduction of C_{60} by N,N -dimethylaniline. The lifetime of the signal is approximately 50 μ s, the same lifetime observed for N,N -dimethylaniline radical cation under the same conditions.

Wudl et al. have shown that C_{60} reacts chemically with primary amines,³² giving various substitution products. Sension et al.²⁸ and Wang³³ have shown that the fullerenes form charge-transfer complexes with N,N -dimethylaniline and N,N -diethylaniline, respectively. Figure 1 was obtained by excitation of C_{60} (presumably both complexed and uncomplexed) in the presence of excess N,N -dimethylaniline, under argon. There was no noticeable change in the visible absorption spectrum of C_{60} at the low amine concentrations used during the quenching studies. However, solutions containing excess triethylamine and tripropylamine showed decreases in the C_{60} absorption between 450 and 700 nm, and then new maxima below 450 nm formed after extended laser excitation.

The free energy for electron transfer to ${}^3C_{60}$ (ΔG_{et}) is calculated from eq 2:

$$\Delta G_{et} = 23.06[E(D^+/D) - E(A^-/A) - \Delta E_{0,0} - e_0^2/a\epsilon] \quad (2)$$

where $E(D^+/D)$ is the oxidation potential of the donor (D, Table I), $E(A^-/A)$ is the reduction potential of the acceptor (A, C_{60}),³⁴ $\Delta E_{0,0}$ is the excitation energy of ${}^3C_{60}$, and $e_0^2/a\epsilon$ is the energy gained in bringing the two radical ions to the encounter distance (a) in a solvent of dielectric constant ϵ , where e_0 is the electronic charge.^{18,35} In benzonitrile, $\epsilon = 25.2$.³⁶

A plot of $\log k_q$ vs ΔG_{et} (Figure 2) gives a fairly good correlation with rate constants calculated for electron transfer using the semiempirical Weller equation¹⁸ (solid line). The general shape of the plot is similar to the shape of the calculated line, which assumes a diffusion rate constant of $2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ in acetonitrile.

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(34) Ferrocene/ferrocenium ion standard is more easily reduced in benzonitrile ($E_1 = 0.50 \text{ V}$) than in CH_3CN (0.41 V).⁴⁶ The reduction potential of C_{60} (-0.42 V vs SCE^{14,46}) was corrected to CH_3CN from benzonitrile using this difference (-0.09 V) to give -0.51 V vs SCE, the value used to calculate the values for ΔG_{et} given in Table I.

(35) The value for $e_0^2/a\epsilon$ in acetonitrile (0.06 eV¹⁸), corrected by the ratio of the dielectric constants,³⁶ is 0.085 eV. Adding this value to -0.51 V for C_{60} gives -0.42 V .^{14,34} Since $\Delta E_{0,0} = 1.56 \text{ eV}$,^{1,3,3,10} the reduction potential of ${}^3C_{60}$ in benzonitrile is 1.14 V vs SCE.

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However, benzonitrile is 3.6 times more viscous than acetonitrile at room temperature,³⁶ and the diffusion rate in benzonitrile calculated from the Stokes–Einstein equation should be $\sim 5.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, in excellent agreement with the maximum rate constants in Table I.³⁷

In conclusion, ${}^3C_{60}$ is a powerful electron acceptor, with a reduction potential near 1.14 V vs SCE. It is reduced by electron donors according to the Weller equation with the formation of aromatic amine radical cations and C_{60} radical anion, which absorbs between 900 and 1120 nm. Further studies of fullerene excited-state redox behavior are in progress.

Acknowledgment. Supported by NSF Grant No. CHE89-11916 and NIH Grant No. GM-20080. We thank F. Wudl et al. and D. Dubois for helpful discussions regarding the reduction potential of C_{60} .

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Self-Assembling Hexameric Helical Bundle Forming Peptides

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Amphiphilic peptides may fold themselves into well-defined secondary structures.¹ DeGrado and other scientists have shown that association of hydrophobic side chains in amphiphilic peptides may lead to the formation of a 4-helical bundle in their 3-dimensional structures.^{2–4} Although synthetic 6-helical-bundle peptides have been a subject of current interest,⁵ their structures

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