mmol) and methyl chlorothioformate (4.9 g, 44 mmol) in 120 mL of methylene chloride. After the addition was completed, the reaction mixture was stirred at room temperature for 11 h. Workup as described above followed by vacuum distillation gave 5.8 g of **8** (71%) as a deep red liquid: bp 100 °C (0.1 torr); IR (neat) 3120 (w), 2935 (w), 2335 (w), 2025 (vs), 1955 (vs), 1815 (m), 1700 (vs), 1650 (s), 1450 (m), 1420 (w), 1375 (m), 1250 (m), 1050 (m), 1030 (m), 945 (w), 830 (s), 670 (m), 635 (s), 625 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.38 (3 H, s, CH_3), 5.09 (2 H, t, $H_{3,4}$), 5.78 (2 H, t, $H_{2,5}$); mass spectrum m/e 277 (M^+).

Anal. Calcd for $C_9H_7NO_4S$: mol wt, 276.9500. Found: mol wt, 276.9484.

(η^5-Carboxycyclopentadienyl)dicarbonylnitrosylchromium (9). [η^5-((Methylthio)carbonyl)cyclopentadienyl]dicarbonylnitrosylchromium (2.0 g, 7.2 mmol) was dissolved in 25 mL of ethanol and the resulting solution diluted with 25 mL of water. Potassium hydroxide (1.14 g, 20.4 mmol) was added and the resulting mixture refluxed for 2 h. The solution was cooled to room temperature and poured into 150 mL of ice water. The aqueous layer was acidified with dilute hydrochloric acid to precipitate the product, which was separated by filtration and dried under high vacuum at room temperature to give 0.89 g (50%) of **9** as a red-brown solid. An analytical sample was obtained by sublimation at 110 °C under high vacuum: mp 193 °C dec; IR (KBr) 2030, 1955, 1705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.30 (2 H, t, $H_{3,4}$), 5.81 (2 H, t, $H_{2,5}$); mass spectrum m/e 247 (M^+).

Anal. Calcd for $C_9H_5CrNO_5$: C, 38.88; H, 2.04; N, 5.67. Found: C, 38.79; H, 2.02; N, 5.62.

[η^5-(Hydroxybenzyl)cyclopentadienyl]dicarbonylnitrosylchromium (12). (η^5-Benzoylcyclopentadienyl)dicarbonylnitrosylchromium (1.0 g, 3.2 mmol) was dissolved in 30 mL of 95% ethanol, sodium borohydride (0.1 g, 2.6 mmol) was added, and the mixture was stirred at room temperature for 1 h. To this solution was added 1 mL of 6 N sodium hydroxide, and the reaction mixture was heated on a steam bath for 15 min. The solution was concentrated by removing approximately half of the solvent under aspirator vacuum; 100 mL of water was then added and the product precipitated. The latter was removed by filtration and dried under high vacuum at room temperature to give 0.8 g (79%) of **12** as a red-orange crystalline solid. An analytical sample was obtained by sublimation under high vacuum: mp 57–58 °C; IR (KBr) 3320 (m), 2005 (s), 1935 (s), 1680 (s), 1260 (m), 1070 (w), 1035 (m), 1005 (m), 795 (m), 735 (m), 700 (m), 625 (s), 465 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.28 (1 H, d, OH), 4.96 (2 H, t, $H_{3,4}$), 5.06 (1 H, q, H_2 or H_5), 5.29 (1 H, q, H_2 or H_5), 5.49 (1 H, d, HCOH), 7.46 (5 H, s, Ph); mass spectrum, m/e 309 (M^+).

Anal. Calcd for $C_{14}H_{11}CrNO_4$: C, 54.37; H, 3.58; N, 4.53. Found: C, 54.50; H, 3.58; N, 4.61.

[η^5-(1-Hydroxyphenethyl)cyclopentadienyl]dicarbonylnitrosylchromium (13). In a manner similar to that described above, [η^5-(phenylacetyl)cyclopentadienyl]dicarbonylnitrosylchromium (0.85 g, 2.6 mmol) was reduced with excess sodium borohydride in 30 mL of 95% ethanol to produce, following workup, 0.50 g (59%) of **13**, mp 52–54 °C. The sample was purified by vacuum sublimation: IR (KBr) 3350 (m), 2020 (vs), 1945 (vs), 1685 (vs), 1400 (m), 1240 (m), 1150 (m), 1050 (m), 845 (m), 820 (m), 760 (m), 730 (s), 690 (s), 665 (m), 625 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.96 (1 H, d, OH), 2.93 (2 H, d, CH_2), 4.52 (1 H, dt, HCOH), 4.91 (3 H, d, $H_{2,3,4}$), 5.19 (1 H, q, H_5), 7.28 (5 H, s, Ph); mass spectrum, m/e 323 (M^+).

Anal. Calcd for $C_{15}H_{13}CrNO_4$: C, 55.73; H, 4.05; N, 4.33. Found: C, 55.91; H, 3.81; N, 4.29.

(η^5-Benzylcyclopentadienyl)dicarbonylnitrosylchromium (24). Method A. Aluminum chloride (0.2105 g, 1.58 mmol) was added slowly to a stirred suspension of lithium aluminum hydride (0.0613 g, 1.62 mmol) in 3 mL of ethyl ether. After the vigorous reaction had subsided, (η^5-benzoylcyclopentadienyl)dicarbonylnitrosylchromium (0.5051 g, 1.64 mmol) in 4 mL of ethyl ether was added dropwise so as to maintain gentle reflux. The reaction mixture was then stirred at room temperature for 10 min, followed by the addition of 10 mL of ice water and 2 drops of concentrated hydrochloric acid. The ether layer was separated, washed twice with water, and dried with magnesium sulfate. The solvent was removed under aspirator vacuum, followed by vacuum distillation to give 0.30 g (59%) of **24**: bp 80 °C (0.01 torr); IR (neat) 2020 (vs), 1945 (vs), 1690 (vs), 1480 (w), 1430 (w), 1025 (w), 925 (w), 820 (w), 760 (w), 705 (m), 635 (s), 625 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.47 (2 H, s, CH_2), 4.80 (4 H, s, H_{2-5}), 7.14 (5 H, s, Ph); mass spectrum, m/e 293 (M^+).

Anal. Calcd for $C_{14}H_{11}CrNO_3$: C, 57.34; H, 3.78; N, 4.78. Found: C, 57.25; H, 3.93; N, 4.77.

Method B. Aluminum chloride (0.2108 g, 1.58 mmol) was added slowly to a stirred suspension of lithium aluminum hydride (0.0656 g, 1.73 mmol) in 3 mL of ethyl ether. After the vigorous reaction had subsided, [η^5-(hydroxybenzyl)cyclopentadienyl]dicarbonylnitrosylchromium (0.5091 g, 1.65 mmol) in 10 mL of ethyl ether was added dropwise so as to maintain a gentle reflux. The reaction mixture was stirred at room temperature for 10 min, followed by hydrolysis with 10 mL of water and 3 drops of concentrated hydrochloric acid. The ether layer was separated and washed twice with water and then dried with anhydrous magnesium sulfate, and the solvent was removed under aspirator vacuum to give 0.2643 g (55%) of **24**, identical with the product described above.

[η^5-(2-Phenylethyl)cyclopentadienyl]dicarbonylnitrosylchromium (25). In a manner similar to that described above, lithium aluminum hydride (0.0613 g, 1.62 mmol) in 3 mL of ethyl ether, aluminum chloride (0.2120 g, 1.59 mmol), and [η^5-(1-hydroxy-2-phenylethyl)cyclopentadienyl]dicarbonylnitrosylchromium (0.5270 g, 1.63 mmol) in 10 mL of ethyl ether were allowed to react to give 0.3056 g (61%) of **25** as a red liquid: bp 80 °C (0.01 torr); IR (neat) 3040 (w), 2940 (w), 2020 (vs), 1945 (vs), 1690 (vs), 1600 (w), 1490 (m), 1445 (m), 1170 (w), 1065 (w), 1020 (m), 955 (m), 820 (s), 745 (s), 690 (s), 660 (s), 635 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.60 (4 H, m, CH_2CH_2), 4.82 (4 H, s, H_{2-5}), 7.20 (5 H, s, Ph); mass spectrum, m/e 307 (M^+).

Anal. Calcd for $C_{15}H_{13}CrNO_3$: C, 58.63; H, 4.23; N, 4.56. Found: C, 58.82; H, 4.26; N, 4.43.

[η^5-(1-Hydroxy-1-methylethyl)cyclopentadienyl]dicarbonylnitrosylchromium (14). A solution of methylmagnesium iodide was prepared from magnesium (0.098 g, 4.0 mmol) and excess methyl iodide in 6 mL of ethyl ether. To this solution was added rapidly (η^5-acetylcyclopentadienyl)dicarbonylnitrosylchromium (0.4995 g, 2.0 mmol) in 5 mL of ethyl ether, and the solution was stirred at room temperature for 1 h. The reaction mixture was hydrolyzed with 10 mL of water, the aqueous and organic layers were separated, and the aqueous layer was extracted with 10 mL of ether. The combined organic layers were washed with water and then dried with anhydrous magnesium sulfate. The solution was filtered and the solvent removed under vacuum to give 0.50 g (94%) of **14**: IR (neat) 3400 (s), 2975 (m), 2025 (s), 1945 (s), 1815 (w), 1675 (s), 1450 (w), 1370 (w), 1260 (m), 1160 (w), 1100 (m), 1030 (m), 950 (w), 790 (m), 640 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.39 (6 H, s, Me), 2.24 (1 H, s, OH), 4.80 (2 H, t, $H_{3,4}$), 5.14 (2 H, t, $H_{2,5}$); mass spectrum, m/e 261 (M^+).

Anal. Calcd for $C_{10}H_{11}CrNO_4$: mol wt, 261.0093. Found: mol wt, 261.0162.

[η^5-(1-Hydroxy-1-phenylethyl)cyclopentadienyl]dicarbonylnitrosylchromium (15). Method A. In a manner similar to that described above, methylmagnesium bromide in 6 mL of ethyl ether was allowed to react with (η^5-benzoylcyclopentadienyl)dicarbonylnitrosylchromium (0.5015 g, 1.63 mmol) in 6 mL of ethyl ether to give upon the usual workup 0.48 g (89%) of **15**. Treatment of **6** as above with methylmagnesium chloride or iodide in the place of methylmagnesium bromide gave **15** in yields of 75% and 95%, respectively: IR (neat) 3500 (m), 2025 (vs), 1950 (vs), 1695 (vs), 1495 (m), 1450 (m), 1410 (w), 1380 (m), 1330 (w), 1170 (m), 1020 (m), 1000 (m), 930 (w), 895 (w), 820 (m), 785 (m), 760 (m), 695 (s), 650 (m), 635 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.76 (3 H, s, Me), 2.20 (1 H, s, OH), 4.83 (2 H, t, $H_{3,4}$), 5.15 (1 H, q, H_2 or H_5), 5.24 (1 H, t, H_2 or H_5), 7.15–7.60 (5 H, m, Ph); mass spectrum, m/e 323 (M^+).

Anal. Calcd for $C_{15}H_{13}CrNO_4$: mol wt, 323.0249. Found: mol wt, 323.0256.

Method B. In a manner similar to that described above, a solution of phenylmagnesium bromide prepared from magnesium (0.0989 g, 4.11 mmol) and bromobenzene (0.6459 g, 4.1 mmol) in 6 mL of ethyl ether was allowed to react with (η^5-acetylcyclopentadienyl)dicarbonylnitrosylchromium (0.4009 g, 1.64 mmol) in 5 mL of ethyl ether to give, upon the usual workup, 0.48 g (89%) of **15** identical with the product obtained above. Treatment of **10** with phenylmagnesium iodide as above gave **15** in 94% yield.

[η^5-(Hydroxydiphenylmethyl)cyclopentadienyl]dicarbonylnitrosylchromium (16). In a manner similar to that described above, phenylmagnesium bromide, prepared from magnesium (0.078 g, 3.2 mmol) and bromobenzene (0.53 g, 3.3 mmol) in 6 mL of ethyl ether, was allowed to react with (η^5-benzoylcyclopentadienyl)dicarbonylnitrosylchromium (0.500 g, 1.6 mmol) in 6 mL of ethyl ether to give, after the usual workup, 0.395 g (64%) of **16** as a red, crystalline solid. An analytical sample was obtained by sublimation under high vacuum at 100 °C: mp 115–116 °C; IR (KBr) 3575 (m), 3400 (m), 2015 (vs), 1935 (vs), 1695 (vs), 1480 (m), 1440 (w), 1315 (m), 1225 (w), 1160 (m), 1080 (m), 1025 (m), 1005 (m), 945 (w), 920 (w), 885 (w), 830 (m), 760 (s), 745 (s), 698 (vs), 664 (m), 625 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.56 (1 H, s, OH), 4.88 (2 H, t, $H_{3,4}$), 5.08 (2 H, t, $H_{2,5}$), 7.22 (10 H, s, Ph); mass spectrum, m/e 385 (M^+).

Anal. Calcd for $C_{20}H_{15}CrNO_4$: C, 62.33; H, 3.92. Found: C, 62.44; H, 4.11.

(η^5-Isopropenylcyclopentadienyl)dicarbonylnitrosylchromium (18). [η^5-(1-Hydroxy-1-methylethyl)cyclopentadienyl]dicarbonylnitrosylchromium (3.31 g, 12.7 mmol), *p*-toluenesulfonic acid (0.60 g, 3.2 mmol), and 10 mg of hydroquinone were dissolved in 100 mL of benzene. The mixture was refluxed for 2 h with continual removal of water, and then the solvent was removed under vacuum. The resulting oil was extracted with hexane and filtered through silica gel by eluting with hexane and then hexane–ether 5:1. The solvent was removed under vacuum to give 2.5 g (81%) of **18** as a red liquid: bp 90–92 °C (0.5 torr); IR (neat) 3100 (w), 2950 (w), 2020 (vs), 1945 (vs), 1695 (vs), 1475 (w), 1440 (w), 1380 (w), 1300 (w), 1160 (w), 1040 (w), 895 (m), 825 (m), 678 (m), 640 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.80 (3 H, d, CH_3), 4.8–5.0 (3 H, m, $H_{3,4}$ and vinyl), 5.1–5.25 (3 H, m, $H_{2,5}$ and vinyl); mass spectrum, m/e 243 (M^+).

Anal. Calcd for $C_{10}H_9CrNO_3$: C, 49.39; H, 3.73; N, 5.76. Found: C, 49.31; H, 3.90; N, 5.94.

[η^5-(2-Formyl-1-chlorovinyl)cyclopentadienyl]dicarbonylnitrosylchromium (26). Phosphorus oxychloride (3.3 mL, 35.5 mmol) was added dropwise to 20 mL of dimethylformamide cooled to 0 °C. To this mixture was added dropwise (η^5-acetylcyclopentadienyl)dicarbonylnitrosylchromium (2.90 g, 11.8 mmol) dissolved in 10 mL of dimethylformamide. The solution was stirred at 0 °C for 15 min and 25 °C for 5 h and then poured into cold sodium acetate solution (20%, 100 mL) and stirred for another 2 h. The mixture was poured into water and extracted thoroughly with methylene chloride. The combined extracts were washed well with water and dried over magnesium sulfate. The solution was filtered, 20 g of silica gel was added, and the solvent was removed under vacuum. The residue was added to a dry-packed column (4 × 8 cm) of silica gel. Elution of the column with ethyl ether gave a red band which upon removal of the solvent under vacuum gave 1.3 g (38%) of **26**. An analytical sample was obtained by several recrystallizations from ethyl ether–hexane to give red plates: mp 106–107.5 °C; IR (KBr) 2020 (s), 1950 (s), 1700 (s), 1650 (s), 1600 (w), 1265 (w), 1115 (m), 930 (w), 820 (w), 615 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.25 (2 H, t, $H_{3,4}$), 5.74 (2 H, t, $H_{2,5}$), 6.45 (1 H, d, olefin), 10.19 (1 H, d, aldehyde).

Anal. Calcd for $C_{10}H_6CrClNO_4$: C, 41.20; H, 2.07; N, 4.80. Found: C, 41.60; H, 2.21; N, 4.63.

(η^5-Ethynylcyclopentadienyl)dicarbonylnitrosylchromium (27). [η^5-(2-Formyl-1-chlorovinyl)cyclopentadienyl]dicarbonylnitrosylchromium (1.0 g, 3.4 mmol) was dissolved in 20 mL of dioxane and heated to reflux. To the refluxing solution was added 20 mL of hot 0.5 N sodium hydroxide solution, and refluxing was continued for an additional 30 min. The solution was poured into ice water, acidified with dilute hydrochloric acid, and extracted into ether. The ether extracts were combined, washed well with water, dried over magnesium sulfate, and filtered. The ether was removed under vacuum to give 0.6 g (77%) of **27** as a red oil: bp 72–75 °C (0.5 torr); IR (neat) 3305 (m), 3020 (w), 2960 (w), 2010 (s), 1975 (s), 1715 (s), 1470 (w), 1255 (w), 830 (m), 640 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.80 (1 H, s, ethynyl), 4.94 (2 H, t, $H_{3,4}$), 5.28 (2 H, t, $H_{2,5}$).

Anal. Calcd for $C_9H_5CrNO_3$: C, 47.57; H, 2.22; N, 6.17. Found: C, 47.55; H, 2.46; N, 5.87.

Determination of the pK_a of (η^5-Carboxycyclopentadienyl)dicarbonylnitrosylchromium (9). Ten-milliliter solutions of 0.003 M (η^5-carboxycyclopentadienyl)dicarbonylnitrosylchromium in water were titrated with 0.5 N sodium hydroxide at 23 °C. The pK_a was obtained experimentally from the titration curve by determining the pH at half-neutralization. The titrations were made on a Radiometer Titrigraph, Type SBR2c, Copenhagen (U.S. distributor, The London Co., Westlake, Ohio) coupled with the Radiometer Titrator II and pH Meter 25 with a combination glass electrode. It was necessary to connect a ground wire from the chassis of the Titrigraph to that of the Titrator II. The Titrigraph was coupled by its flexible drive shaft to a 0.5-mL syringe which delivered the titrant into the stirred sample. The pK_a was determined to be 5.1 ± 0.15.

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Transition-Metal-Catalyzed Reactions of Diazo Compounds. 1. Cyclopropanation of Double Bonds

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Rhodium(II) and palladium(II) carboxylates are efficient catalysts for the cyclopropanation of olefins by diazo esters. Intramolecular competitions within diolefins and intermolecular competitions between pairs of monoolefins showed quite different cyclopropanation selectivities with the above-mentioned metal derivatives. Rhodium essentially promotes a carbenoid mechanism involving an electrophilic attack of uncomplexed olefins, while a determinant olefin coordination is observed with palladium. By comparison, the classical copper derivatives are essentially borderline cases: most often they behave as carbenoid catalysts, except when associated with very weak ligands such as in copper triflate. The synthetic usefulness of these reactions is emphasized in terms of their high efficiency and regioselectivity.

The reactions of carbenes or carbenoids generated by metal-catalyzed decomposition of diazo compounds are now of major synthetic importance. The historical significance of copper catalysis in this field needs no em-

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phasis,[1] although a variety of metal species[2] promotes the cyclopropanation of olefins to some extent. This dominance by copper has been strongly challenged by the recent introduction of some group 8 metals[3] that appear to be synthetically useful. The relevance of metal–olefin coordination in the copper-catalyzed cyclopropanation has been extensively discussed. As the understanding of the reaction developed, it appeared that two different mechanisms might be involved, possibly as competitive pathways, one for which metal–olefin coordination is a key factor and the other a bimolecular process with metal–carbenoid species attacking uncomplexed olefins. Kochi's recent work[4] indicated the former type of mechanism to be operative in the particular case of copper(I) trifluoromethanesulfonate (copper triflate, CuTf). In order to gain a further understanding of these reactions and also to widen their synthetic utility, we have undertaken a systematic search for new catalysts. With the hope of diversifying the selectivities, we have been testing the following general types of metal complexes: (a) complexes containing only one single coordination site per metal (in order to favor carbenoid reactions), and (b) complexes with several available sites for strong coordination of olefins (in order to promote coordination reactions).

Results and Discussion

A. The Catalysts. After screening many examples, rhodium(II) carboxylates and palladium(II) derivatives were tentatively retained as models of type a and b catalysts, respectively. They were compared with $CuTf_2$, a recently introduced and efficient catalyst[5] for the cyclopropanation of olefins.

Rhodium(II) carboxylates are diamagnetic complexes with only one coordination site per metal.[6] They form stable adducts with basic ligands but not with olefins. On the contrary, the propensity of palladium derivatives to complex olefins is well-known.[7] Because of the extraordinarily poor coordinating ability of triflate anions, copper triflate seems particularly suited to promote the complexation of other ligands, especially in its reduced form [Cu(I)]. Each metal complex used in this study is air stable, promotes a fast decomposition of diazo esters at room temperature, and is at least moderately soluble in olefins (see Experimental Section). Hereafter, Pd-CH_3, Rh-CH_3, Rh-Piv, Rh-*n*-Bu, and Rh-CF_3 are used as abbreviations for the corresponding carboxylates (CH_3 indicates the acetate, Piv the trimethylacetate (pivalate), *n*-Bu the butyrate, and CF_3 the trifluoroacetate).

Table I. Efficiency of Some Catalysts in the Cyclopropanation of Styrene with Ethyl Diazoacetate (EDA)[a]

catalyst	yield,[b] %	trans/cis ratio[c]
$PdCl_2$	70	
$Pd(O_2CCH_3)_2$	98	2.0
$PdCl_2 \cdot 2PhCN$	65	2.3
$Pd(PPh_3)_4$	57	2.2
Pd on C	0	
$Cu(acac)_2$	65	2.1
$RhCl_3 \cdot 3H_2O$	7	
$RhCl(PPh_3)_3$	12	
$Rh_2(O_2CCH_3)_4$	92	1.5
$Rh_2(O_2C\text{-}t\text{-}C_4H_9)_4$	60	1.5
$Rh_2(O_2C\text{-}n\text{-}C_6H_{13})_4$	95	1.3
$Rh_2(O_2CCF_3)_4$	66	0.9
$Mo_2(O_2CCH_3)_4$	5	
$Ru_2(O_2CCH_3)_4Cl$	38	1.8

[a] Reaction conditions: 22 °C; styrene, 3×10^{-2} mol; catalyst, 10^{-5} mol; diazo ester, 2×10^{-3} mol. Abbreviations (for all the tables): MDA, EDA, and BDA refer respectively to methyl, ethyl, and *n*-butyl diazoacetate. [b] Mixture of ethyl *cis*- and *trans*-2-phenylcyclopropanecarboxylate; yields based on EDA. [c] Ratio of area in the GLC peaks.

No modifications of the metal oxidation state were detected by EPR after addition of ethyl diazoacetate (EDA) to solutions of palladium(II) and rhodium(II) acetates in 1-octene and in styrene.[8] In contrast with $CuTf_2$ as catalyst, we observed the disappearance of the EPR signals of the Cu(II) ions. Although the occurrence of Cu(II) species at the active catalytic site is well documented in several cases,[9] our findings are in agreement with Kochi's results[4] and also with our previous EPR and polarographic observations that EDA reduces Cu(II) to Cu(I) in unsaturated nitriles.[10]

B. Relative Efficiencies of the Catalysts. Table I shows the results of the cyclopropanation of styrene with a variety of metal derivatives as catalysts. Cu-Tf_2, Pd-CH_3, and rhodium(II) carboxylates are among the most efficient complexes for this reaction. In contrast, Table II shows that Pd-CH_3 is not very efficient for the cyclopropanation of internal olefins (entries 2–8, best yields below 25%) or of dienes (entries 20–24, best yields below 40%). Nevertheless, some 4-substituted styrenes (entries 27–31) and strained cyclic or bicyclic olefins such as cyclopentene, norbornene (NB), or norbornadiene (NBD) are notable exceptions to this generalization.

Rh-CH_3 very efficiently catalyzes the cyclopropanation of mono- as well as polyolefins, substituted or not (Table II and ref 3i). Internal strain has little or no effect. Cis olefins give somewhat better yields than their trans isomers but with a strong dependence on the catalyst counterion[3i]

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(8) With the present evidence, we cannot exclude a reduction to low-valent species since Rh(I) complexes are diamagnetic (d^8) and all known Pd(I) complexes binuclear and diamagnetic [see W. E. Geiger, Jr., C. S. Allen, T. E. Mines, and F. C. Senftleber, *Inorg. Chem.*, **16**, 2003 (1977)].

(9) D. S. Wulfman, B. G. McGibboney, E. K. Steffen, N. V. Thinh, R. S. McDaniel, and B. W. Peace, *Tetrahedron*, **32**, 1257 (1975).

(10) P. G. Moniotte, A. J. Hubert, and P. Teyssié, *J. Organomet. Chem.*, **88**, 115 (1975). See also: D. Bethell, K. L. Handoo, S. A. Fairhurst, and L. H. Sutcliffe, *J. Chem. Soc., Chem. Commun.*, 326 (1977); T. Saegusa, Y. Ito, T. Shimizu, and S. Kobayashi, *Bull. Chem. Soc. Jpn.*, **42**, 3535 (1969); T. Shirafuji, Y. Yamamoto, and H. Nozaki, *Tetrahedron*, **27**, 5353 (1971).

(11) D. E. James and J. K. Stille, *J. Am. Chem. Soc.*, **98**, 1806 (1976).

Table II. Relative Efficiency of Pd, Cu, and Rh Catalysts for the Cyclopropanation of Olefins by Diazo Esters[c]

entry	olefin	diazo ester	yield, % $Pd(O_2CMe)_2$	yield, % $CuTf_2$	yield, % $Rh_2(O_2CMe)_4$
1	1-hexene	MDA	30	36	86
2	*cis*-2-butene	MDA	24		54
3	*trans*-2-butene	MDA	21		
4	*cis*-3-hexene	MDA			56
		EDA	15	15	
		BDA			98
5	*cis*-2-octene	MDA	5	40	65
		BDA			90
6	*trans*-2-octene	MDA	2	14	24
		BDA			70
7	*trans*-4-octene	MDA	12	8	7
		BDA			70
8	2,3-dimethyl-2-butene (TME)	EDA	5	30	70
9	cyclopentene	EDA	60	60	95
10	cyclohexene	MDA	15		80
		EDA	21	54	88
		BDA	19		89
11	cycloheptene	EDA	40	30	75
12	cyclooctene	EDA	20	28	95
13	styrene	EDA	98	80	90
14	indene	EDA	20	55	71
15	norbornene	EDA	87	95	95
16	vinyl acetate	EDA	5	22	77
17	ethyl vinyl ether	EDA	42	0[a]	85
18	dimethyl maleate	EDA	traces	traces	traces
19	dihydropyran	EDA	20	55	71
20	1,3-pentadiene	EDA	35, 13[b]	66, 16[b]	73, 23[b]
21	isoprene	EDA	37, 11[b]	25, 49[b]	36, 57[b]
22	1,5-hexadiene	EDA	37	60	80
23	1,3-cyclohexadiene	EDA	18	53	90
24	1,5-cyclooctadiene (COD)	EDA	10	25	64
25	norbornadiene (NBD)	EDA	95	47	88
26	α-methylstyrene	EDA	42		
27	4-methylstyrene		81		
28	4-methoxystyrene		79		
29	4-chlorostyrene		86		
30	4-nitrostyrene		77		
31	2-nitrostyrene		73		
32	4-(dimethylamino)styrene		0		
33	1,1-diphenylstyrene		0		
34	*trans*-1,2-diphenylstyrene		0		
35	4-vinylpyridine		0		
36	1-vinylimidazole		0		

[a] The starting material polymerizes. [b] Respectively for mono- and disubstituted double bond. [c] Same experimental conditions as in Table I.

and on the diazo ester used (Table II, entries 4–7). In general, butyl diazoacetate (BDA) gives better results than its lower homologues methyl and ethyl diazoacetates (MDA and EDA, respectively).

Copper triflate usually displays an intermediate efficiency when compared to the other catalysts (Table II, entries 1, 5, 10, 19, 24).

C. Palladium. Importance of Olefin Coordination. The most striking differences in selectivities of palladium-catalyzed cyclopropanations are observed in intermolecular competitions between olefins of different coordinating power. Those results are summarized in Table III. The overall trend observed in noncompetitive experiments is confirmed: strained olefins (Table III, entries 1, 3, 5, 13, 16) or conjugated olefins such as styrene are preferred in competitions. Terminal alkenes are more reactive than internal isomers or homologues (entries 4, 6, 7, 9). In intramolecular competitions, the less substituted bond is regioselectively cyclopropanated, as expected from steric requirements for a mechanism involving initial π complexation of the olefinic substrate (Table II, entries 20 and 21; ratios of mono- to disubstituted double bonds cyclopropanated are 1,3-pentadiene = 2.7 and isoprene = 3.4).

The scope and limitations of Pd-catalyzed cyclopropanations are further detailed in Table IV. Together with the competition results, Table IV quotes the complexation constants, *K*, with silver for the olefins,[12] as well as their rate constants, *k*, for 1,3-dipolar addition with picryl azide.[13] It is apparent that for an olefin, a high *K* value corresponds to a high reactivity toward carbene addition (but for 1,5-cyclooctadiene, vide infra). Accordingly, Figure 1 plots a few examples of olefin coordination constants *K* with Ni(0)[14] against their relative reactivities in competitive cyclopropanations. Here also, a direct relationship between reactivity and coordinating ability is clearly evidenced. Besides, the relative reactivity of cyclic olefins approximately follows the same order as that observed by Stille for olefin carbonylation, a Pd-catalyzed reaction which is clearly π-complex controlled.[11]

Figure 2 plots the results of Pd- and Rh-catalyzed competitions between various olefins and 1-hexene against the

(12) Because of the scarcity of palladium–olefin formation constants, values for Ag complexes were used instead in Table IV. However, the decrease of π-complex stability caused by substitution of the double bond is more significant with Pd, and steric effects should accordingly play a greater role in Pd-catalyzed reactions. (a) M. A. Muhs and F. T. Weiss, *J. Am. Chem. Soc.*, **84**, 4697 (1962). (b) F. R. Hartley, *Chem. Rev.*, **73**, 163 (1973). (c) W. Partenheimer, *J. Am. Chem. Soc.*, **98**, 2779 (1976).

(13) A. S. Bailey and J. E. White, *J. Chem. Soc. B*, 819 (1966).

(14) C. A. Tolman, *J. Am. Chem. Soc.*, **96**, 2780 (1974).

Table III. Competitive Cyclopropanations between Olefins in the Presence of Palladium(II) Acetate, Copper(II) Triflate and Rhodium(II) Acetate[a]

entry	diazo ester	olefin A	catalyst[b] Pd (ΔB/ΔA)	Cu (ΔB/ΔA)	Rh (ΔB/ΔA)	olefin B
1	MDA	1-hexene	6.7 (6:40)	4.2 (4:17)	1.5 (21:31)	norbornene
2			1.0 (38:38)	2.1 (13:28)	5.7 (10:57)	dihydropyran
3			1.2 (17:21)	1.4 (21:30)	1.7 (26:45)	cyclopentene
4			0.1 (10:1)	1 (8:8)	2.0 (19:38)	cyclohexene
5	EDA		1.3 (13:17)	2 (6:12)	1 (39:41)	cycloheptene
6			0.21 (19:4)	0.21 (21:4.5)	0.21 (48:10)	*trans*-4-octene
7			0.33 (18:6)	1.3 (15:20)	1.3 (43:55)	*cis*-2-octene
8			0.86 (29:25)	0.44 (48:21)	0.85 (48:41)	1-dodecene
9			0.12 (23:3)	0.36 (19:7)	0.61 (41:25)	TME[c]
10			1.8 (30:54)	1.9 (32:60)	2.1 (32:66)	styrene
11	MDA	1-octene	0.09 (22:2)	0.7 (23:16)	3.0 (18:53)	vinyl acetate
12			0.13 (7.5:1)	1.7 (3:5)	2.2 (16:36)	1-hexyne
13		1,5-cyclooctadiene	10.5 (4:42)	1.4 (14:20)	0.64 (36:23) 0.95 (36:34)[d]	norbornene
14			53 (1:53)	1.5 (17:26)	1.6 (30:48)	norbornadiene
15	EDA	*trans*-4-octene	2.1 (6:13)	1.5 (16:24)	3.7 (16:60)	*cis*-3-hexene
16	EDA	cyclohexene	87 (1:87)			norbornene
17		styrene	0.9 (32:37)	0.7 (39:28)	0.66 (53:35)	*p*-chlorostyrene
18			1.0 (35:33)	0.7 (45:33)	0.64 (56:36)	*p*-methylstyrene

[a] Experimental conditions: same as in Table I except that there is 2×10^{-2} mol of each olefin. [b] ΔB/ΔA = yield ratio of cyclopropanation products of olefins A and B. The values in parentheses correspond to the yields (%) of the corresponding cyclopropanes, respectively, for olefins A and B. [c] TME = 2,3-dimethyl-2-butene. [d] One mole of monoolefin for each 0.5 mol of diolefin.

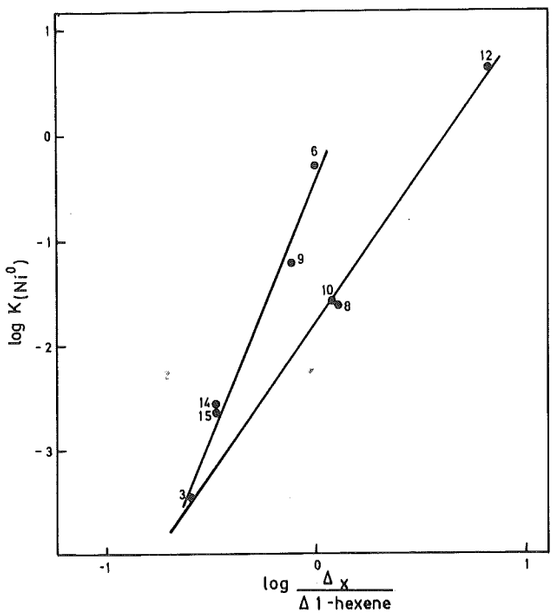


Figure 1. Correlation between coordination constants on nickel(0)[14] and relative reactivities of olefins for Pd-CH_3 catalyzed cyclopropanations: (14) K for *trans*-2-hexene, X = *trans*-2-octene; (15) K for *cis*-2-hexene, X = *cis*-2-octene; the other numbers refer to the olefins reported in Table I.

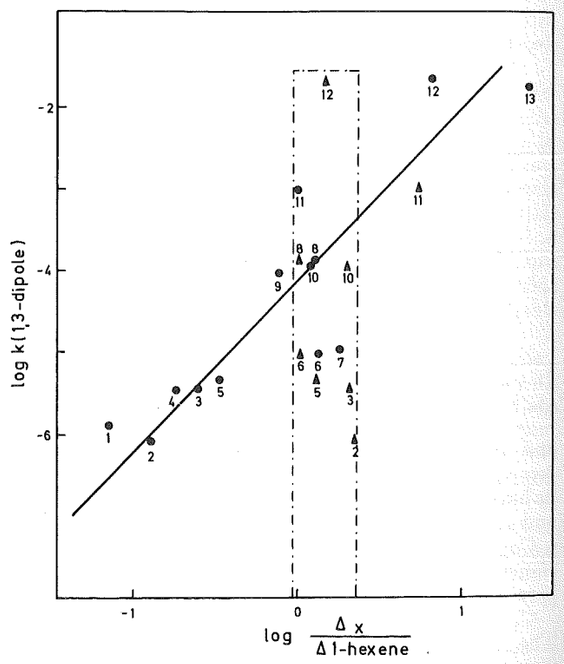


Figure 2. Correlation between the 1,3-dipolar reactivity of olefins (toward picryl azide) and the relative rates of the palladium (●) and rhodium acetate (▲) catalyzed cyclopropanations: (1) vinyl acetate, (2) 1-hexyne, (3) cyclohexene, (4) 1,5-cyclooctadiene, (5) *cis*-2-octene, *trans*-2-octene, and *trans*-4-octene, (6) 1-hexene, (7) styrene, (8) cycloheptene, (9) cyclooctene, (10) cyclopentene, (11) 4,5-dihydropyran, (12) norbornene, (13) norbornadiene.

dipolarophilicity of the same olefins.[13] It shows a correlation between k (1,3-dipole) for an olefin and the relative reactivity of the olefin against 1-hexene for the Pd catalysts. On the contrary, Rh promotes a practically random attack of the olefins, further evidence that the two types of catalysis proceed through basically different mechanistic pathways.

Upon addition of 3 mol % (relative to the olefin) of methyl maleate or fumarate to the otherwise quite reactive styrene or norbornene, a sharp drop in the yields of cyclopropanes is observed. The decrease in yield is related to the coordinating ability of the diester which is greater for the cis (maleate) than the trans (fumarate) olefinic inhibitor (cf. neat styrene, 95% cyclopropanation; styrene plus 3 mol% of ethyl maleate, 49%; styrene plus 3 mol % of ethyl fumarate, 72%; neat norbornene, 87%; norbornene plus 3 mol % of ethyl maleate, 77%). Therefore, maleate and fumarate effectively compete with the olefins and the diazo ester for coordination to palladium.

It is also evident that chelating diolefins do not follow the same trend as conjugated olefins or monoolefins:

Table IV. Competitive Cyclopropanations between 1-Hexene and Olefin X Catalyzed by Palladium Acetate[a]

olefin X	yield of cyclopropane, % 1-hexene	X	X:1-hexene ratio	K_{Ag^+}[b]	k (1,3-dipole)[c]
1-hexene	30		1	4.3	1.0×10^{-5} [d]
1-dodecene	29	25	0.36		6.6×10^{-5} [d]
trans-4-octene	19	4	0.21	0.5	
trans-2-octene	15	5	0.33	0.4	4.61×10^{-6} [e]
cis-2-octene	18	6	0.33	2.2	
styrene	30	54	1.8	14	1.05×10^{-5}
tetramethylethylene	23	3	0.12	0.1	
cyclopentene	17	21	1.2	7.3	1.08×10^{-4}
cyclohexene	24	6	0.25	3.6	2.55×10^{-6}
cycloheptene	13	17	1.3	12.8	1.36×10^{-4}
cyclooctene	11	8.5	0.76	14.4	9.32×10^{-5}
norbornene (NB)	6	40	6.4	62	2.04×10^{-2}
norbornadiene (NBD)	1.5	37	26	33.7	1.70×10^{-2}
1,5-cyclooctadiene (COD)	30	5.5	0.19	75.0	3.47×10^{-6}
vinyl acetate[f]	22	1.5	0.07		1.29×10^{-6}
1-hexyne[f]	7.5	1.0	0.12		7.88×10^{-7}
dihydropyran	38	38	1.0		9.59×10^{-4}

[a] Same experimental conditions as in Table I except that there is 2×10^{-2} mol of each olefin. [b] From ref 12. [c] From ref 13. [d] Values for 1-pentene and 1-octene, respectively. [e] Value for "2-octene", isomer not precisely known. [f] Competition with 1-octene instead of 1-hexene.

1,5-cyclooctadiene (COD) is only poorly cyclopropanated (either neat or in competition) relative to norbornadiene (NBD, Table II, entries 24 and 25, and Table III, entry 14), although the heats of reaction of these two olefins with bis(benzonitrile)palladium dichloride appear to be very similar.[15]

Rather, the reactivity of a bidentate olefin is related to the presence of at least one strained double bond. The poor reactivity of chelating cycloolefins toward cis attack has been attributed[16] to the inability of the chelate to rotate 90° from a position perpendicular to the square plane of the metal complex to a position which would favor cis addition of the carbene to a ligand attached to the metal. The above statement is not in opposition with the difference in reactivity between strained diolefins (such as NBD) and a true chelating one (COD), as the solutions of complexes of the former consist of mixtures of mono- and dicoordinated species.[14] The mono species could account for the difference in reactivity with true chelates.[17]

Furthermore, a mechanism in which a palladium-coordinated carbene (or diazo ester) reacts with an olefin coordinated to the same metal in a fashion reminiscent of a "cis rearrangement" (possibly via the formation of a metallacyclobutane) fits best the data at hand.

D. Rhodium. Importance of Out-of-Sphere Carbenoid Reactions. Rhodium catalysts are extremely efficient for cyclopropanating almost any kind of alkene (Table II). The lack of reactivity of electron-poor olefins (e.g., methyl maleate) is a notable exception. The substrate-coordinating ability and/or dipolarophilicity have little or no effect (Figure 1). In intermolecular competition studies, Rh catalysts are poorly discriminating, even between strained and unstrained olefins (Table III, entries 1, 13, 14). This behavior is reminiscent of purely electrophilic reactions.[19] The high reactivity of electron-rich olefins (Table III, entries 2, 12) and the preference for cis-disubstituted over terminal olefins in competitions (Table III, entries 4, 7) are all indicative of the importance of electronic factors. Steric factors are not determinant, even if they are effective to some extent (Table III, entries 9, 15).

Table V. Competition between Styrene (S) and Norbornene (NB)[a]

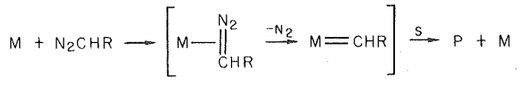
catalyst	yield, % cyclopropanated S	cyclopropanated NB	S:NB ratio
$Rh_2(O_2CCF_3)_4$	19	4	4.75
$Cu(acac)_2$	30	7	4.29
$Cu^{II}(Tf)_2 \cdot 4PPh_3$	33	10	3.3
$Cu^{II}(Tf)_2 \cdot 10PPh_3$	21	7	3
$Rh_2(O_2CCH_3)_4$	65	26	2.5
$Cu^{II}(Tf)_2$	34	53	0.64
$Cu^{I}Tf$[b]	26	41	0.63
$Cu^{I}Tf$[c]	11	45	0.24
$Pd(O_2CCH_3)_2$	11	85	0.13

[a] Same experimental conditions as in Table I except that there is 2×10^{-2} mol of each olefin; the diazo ester is EDA. [b] Catalyst prepared according to ref 4, 1.1×10^{-4} mol. [c] 2.2×10^{-4} mol.

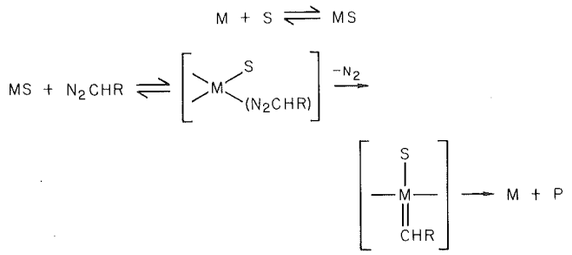
The difference between Rh-CH_3 and Pd-CH_3 is further illustrated by the results of intramolecular competitions in conjugated dienes. With Rh-CH_3, the electron-rich double bond (monosubstituted in 1,3-pentadiene and disubstituted in isoprene;[18] Table II, entries 20, 21) is regioselectively cyclopropanated (different with Pd-CH_3, see section C). Since rhodium(II) carboxylates have only one vacant coordination site per metal, a simultaneous coordination of the olefin and diazo ester (or carbene) seems unlikely. The above facts can be accommodated by postulating an attack of an electrophilic carbenoid by the olefin. Support for this mechanism comes from the apparent activation parameters of the Rh-CH_3 catalyzed cyclopropanation of styrene by EDA. We find that the

(15) W. Partenheimer, *Inorg. Chem.*, **11**, 743 (1972).
(16) D. E. James, L. F. Hines, and J. K. Stille, *J. Am. Chem. Soc.*, **98**, 1810 (1976).
(17) Interestingly, the reactivity of chelated substrates was shown by NMR not to be important, even in the presence of a significant excess of diazo ester (up to 4 times the stoichiometric amount). When MDA is added to a solution of η^3-allylpalladium chloride dimer, $PdCl_2$·COD, or $[RhCl(NBD)]_2$, the signals of the ligands are not modified unless a large excess of MDA is used. Moreover, the last two catalysts decompose the diazo compound at very different rates. $PdCl_2$·COD is practically inactive at −10 °C whereas the rhodium complex promotes the decomposition at −40 °C, although forming only methyl maleate and fumarate and polycarbalkoxycarbenes, even in the presence of olefins.
(18) G. L. Nelson and E. A. Williams, *Prog. Phys. Org. Chem.*, **12**, 288 (1976); O. Kajimoto and T. Fueno, *Tetrahedron Lett.*, 3329 (1972).
(19) K. D. Bingham, G. D. Meakins, and G. H. Whitham, *J. Chem. Soc., Chem. Commun.*, 445 (1972). These authors observed that whereas the *electrophilic* peracids do not discriminate between NB and cyclohexene, 1,3-dipolar addition of an azide is by opposition very selective.

Scheme I



Scheme II



reaction is first order in catalyst with $\Delta H^{\ddagger} = 15.0 \pm 0.6$ kcal mol^{-1} and $\Delta S = -3.1 \pm 2$ eu (0 °C). (See the Experimental Section for details.) This apparent entropy of activation is much higher than that reported for the cyclopropanation of 1-hexene with CuTf[4] (−8.9 eu at −18 °C), a system in which olefin coordination rather than carbene reactivity largely determines selectivity, and very much higher than the value reported for the formal dimerization of carbene under the influence of Pd-CH_3 (−30 eu at 25 °C); it thus provides further support for a carbenoid mechanism.

E. Copper. A Borderline Case. Copper triflate induces selectivities intermediate between those of the two other catalytic systems (e.g., see entries 1–4 and 9–13 in Table III), being, however, closer to Rh in its general pattern. This behavior is best explained by postulating a progressive inhibition of the coordination pathway by an increase of the electron density at the metal level due to basic byproducts. The above supposition is supported by the results of competitions between NB and styrene (Table V). There, in purely carbenoid mechanisms (e.g., with Rh-CH_3 or Cu(acac)$_2$), styrene is definitely preferred to NB, but the selectivity is reversed in favor of the more strongly coordinated NB when coordination mechanisms take over. This is clearly the case with palladium acetate and Cu^{I}Tf. With the latter catalyst, an increase in metal concentration also promotes an enhanced selectivity for the more complexed olefin. Cu^{II}Tf$_2$ shows a selectivity close to that of its reduced form, further proof that the actual catalysts are Cu(I) species, but exhibits a reversal of selectivity (with somewhat lower yields) after addition of strong ligands (PPh_3).

Conclusions

Schematically, our results may be explained by two fundamental mechanistic pathways: a carbenoid mechanism as shown in Scheme I and a coordination mechanism as shown in Scheme II (where M = metal complex, S = unsaturated substrate, and P = products).

Rhodium(II) carboxylates act exclusively according to Scheme I, while palladium carboxylates probably react according to Scheme II. Copper catalysts generally display a carbenoid (Scheme I) type of behavior, with the exception of some complexes carrying weak ligands, notably copper triflates, where the contribution from the mechanism of Scheme II becomes important. Both types of mechanism may, of course, contribute to some extent to the overall process in certain cases (e.g., progressive inhibition of the coordinating ability of the complex). Rhodium carboxylates are very efficient cyclopropanation catalysts, and are only slightly sensitive to strain, coordinating ability, and steric factors. They are particularly well suited for the cyclopropanation of disubstituted isolated double bonds. They are, moreover, very interesting for the study of the preparation of cyclopropenes from acetylenes,[20] the insertion into OH, SH, and NH bonds,[21] and even the insertion into OH bonds of unsaturated molecules.[20,22]

Palladium catalysts are just the opposite. They are exceedingly sensitive to the steric effects of the substrate and in fact will only satisfactorily cyclopropanate monosubstituted activated or strained cyclic double bonds.

Table VI

[styrene], M	10^3[Rh-CH_3], M	[N_2CH-CO_2Et], M	T, K	$10^3 k_{obsd}$, s^{-1}
8.7	1.5	0.115	261	0.38
8.7	1.5	0.115	263	0.45
8.7	1.5	0.115	273	1.12
8.7	0.6	0.115	276	0.60
8.7	1.0	0.115	276	1.03
8.7	1.5	0.115	276	1.44
8.7	1.8	0.115	276	1.75
8.7	2.0	0.115	276	1.98
8.7	1.5	0.115	298	12.93

Experimental Section

Analysis and purification of the cyclopropanes were run on Varian 1700 and 2800 gas–liquid chromatographs (catharometers, W filaments) using analytical (4 ft × $^1/_4$ in.) and preparative (10 ft × $^3/_8$ in.) columns (SE-30 or FFAP, 15% on Chromosorb W, acid washed). The carrier gas was He (40 mL/min). The temperature program was from 70 up to 230 °C (15 °C/min). The olefins were carefully distilled under nitrogen. Most reactions were carried out under nitrogen at room temperature, but with rhodium carboxylates and palladium acetate, there was no distinguishable difference when they were run in air. Boiling points are uncorrected. Palladium acetate and chloride from Johnson-Matthey were used without further purification. Rhodium(II) carboxylates[6] and copper(II) triflate[5] were prepared by methods in the literature. The Cu and Rh catalysts were generally poorly soluble in the olefins but were readily dissolved after addition of a few drops of the diazo ester. After the absence of any absorption at 2175 cm^{-1} (diazo group) was checked, the reaction product was analyzed by GLC using an internal standard (dibutyl or diamyl phthalate, dibutyl, diethyl, or dimethyl maleates or fumarates). The results are summarized in Tables III, IV and V.

Synthesis of Cyclopropanecarboxylates. The same general procedure as above was applied for preparative experiments. After addition of the diazo ester, the reaction mixture was distilled under reduced pressure. The yields and ratios of cis to trans isomers were determined by VPC. On FFAP columns, shorter retention times for the cis rather than the trans isomers were the rule. Analytical samples were purified by adsorption chromatography on silica gel or preparative VPC and were analyzed by NMR and IR. Cyclopropanes were identified with authentic samples when previously described.[3i,25] In some cases, isomeric ratios could not be measured because of poor VPC separation and ambiguous NMR analysis. Spectroscopic data are then given for mixtures of isomers.

Kinetics of the Rh-CH_3 Catalyzed Cyclopropanation of Styrene with Ethyl Diazoacetate. A 25-mL two-necked flask containing the olefin (10 mL) and the catalyst was connected to a measuring buret filled with oil. The other neck was fitted with a rubber septum. The apparatus was immersed in a thermostated glycol–water bath maintained to ±0.2 °C. An approximately 0.7 M solution of EDA in styrene was then added with vigorous stirring through the side neck with a syringe. N_2 evolution began immediately. The quantity of gas evolved was measured at atmospheric pressure with an estimated accuracy of ±0.1 mL. Typical experiments in neat styrene gave linear apparent rate constants as a function of temperature up to 75–80% of reaction. Errors in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated by a least-squares linear-regression analysis. Experimental results are summarized in Table VI.

Methyl 2-(*p*-Methoxyphenyl)cyclopropanecarboxylate. MDA was added to *p*-methoxystyrene according to the general procedure (see above; catalyst Pd–CH_3). Distillation afforded the pure cyclopropanes as a mixture of cis and trans isomers: bp 111 °C (0.01 torr); NMR (CCl_4, Me_4Si) δ 6.8 (m, 4 H, Ph), 3.64 (s, 3 H, OCH_3), 3.56 (s, $COOCH_3$ trans), 3.30 (s, $COOCH_3$ cis) (trans and cis, 3 H), 1.0–2.5 (m, 4 H, cyclopropane). Anal. ($C_{12}H_{14}O_3$): C, H.

Methyl 2-(*p*-methylphenyl)cyclopropanecarboxylate was prepared from *p*-methylstyrene and MDA (catalyst Pd-CH_3): bp 130 °C (0.01 torr); NMR (CCl_4, Me_4Si) δ 7 (m, 4 H, Ph), 3.6 (s, $COOCH_3$ trans), 3.32 (s, $COOCH_3$ cis) (trans and cis, 3 H), 2.3 (s, 3 H, CH_3), 1–2.5 (m, 4 H, cyclopropane). Anal. ($C_{12}H_{14}O_2$): C, H.

Methyl 2-(*p*-chlorophenyl)cyclopropanecarboxylate was prepared from *p*-chlorostyrene and MDA (catalyst Pd-CH_3): bp 140 °C (0.01 torr); NMR (CCl_4, Me_4Si) δ 7.12 (m, 4 H, Ph), 3.60 (s, $COOCH_3$ trans), 3.30 (s, $COOCH_3$ cis) (trans and cis, 3 H), 1–2.5 (m, 4 H, cyclopropane). Anal. ($C_{11}H_{11}O_2Cl$): C, H.

Methyl 2-(*o*- and *p*-nitrophenyl)cyclopropanecarboxylates were obtained from *o*- and *p*-nitrostyrenes and MDA (catalyst Pd-CH_3). These compounds could not be isolated in an analytically pure state, but their identification was possible by NMR spectroscopy.

Methyl 2-(*o*-nitrophenyl)cyclopropanecarboxylate: bp 140–170 °C (0.01 torr); NMR (CCl_4, Me_4Si) δ 7.70 (m, 4 H, Ph), 3.64 (s, $COOCH_3$ trans), 3.38 (s, $COOCH_3$ cis) (trans and cis, 3 H), 1–2.5 (m, 4 H, cyclopropane).

Methyl 2-(*p*-nitrophenyl)cyclopropanecarboxylate: bp 180–210 °C (0.01 torr); NMR (CCl_4, Me_4Si) δ 7.65 (m, 4 H, Ph), 3.68 (s, $COOCH_3$ trans), 3.40 (s, $COOCH_3$ cis) (trans and cis, 3 H), 1–2.5 (m, 4 H, cyclopropane).

***n*-Butyl 2-*n*-decylcyclopropanecarboxylate** was prepared from 1-dodecene and BDA (catalyst Rh-CH_3); bp 100–110 °C (0.01 torr). Analytical purity was obtained by adsorption chromatography on silica gel (elution with *n*-hexane followed by benzene): NMR (CCl_4, Me_4Si) δ 3.95 (t, J = 6 Hz, 2 H, OCH_2), 1–1.9 (m, 32 H, remaining H); mass spectrum (70 eV) m/e (relative intensity) 282 (0, M^+), 209 (2, $M^+ - C_4H_9O$), 173 (17), 155 (36), 117 (56), 99 (100). Anal. ($C_{18}H_{34}O_2$): C, H.

***n*-Butyl 2-acetoxycyclopropanecarboxylate** was prepared from vinyl acetate and BDA (catalyst Rh-CH_3); bp 75 °C (0.01 mm). Analytical purity was obtained by adsorption chromatography on silica gel (elution with *n*-hexane followed by benzene) or by preparative GLC: IR (liquid film) 1750 (acetoxy C=O), 1725 (ester C=O), 1235 (acetoxy C—O), 1176 (ester C—O) cm^{-1}; NMR (CCl_4, Me_4Si) δ 4.0–4.2 (m, 1 H, CH—O cyclopropane), 3.88 (t, J = 6 Hz, 2 H, O—CH_2), 1.82 (s, 3 H, $OOCH_3$), 1.8–0.8 (m, 10 H, remaining H; mass spectrum (70 eV) m/e (relative intensity) 201 (0.6, $M^+ + 1$), 158 (6, $M - CH_3CO + 1$), 129 (56, $M - CH_3 - C_4H_9 + 1$), 127 (8, $M - C_4H_9O$), 103 (16), 102 (17), 85 (32), 84 (27), 73 (100, C_4H_9O). Anal. ($C_{10}H_{16}O_4$): C, H.

Ethyl 2-ethoxycyclopropanecarboxylate was prepared from ethyl vinyl ether and EDA (catalyst Rh-CH_3): bp 64 °C (15 mm); ratio of cis to trans = 0.5; NMR ($CDCl_3$, Me_4Si) δ 4.13 (2 q, J = 7 Hz, 2 H), –C(O)OCH_2, cis and trans), 3.60 (2 q, J = 8 Hz, 2 H, O–CH_2, cis and trans), 0.90–1.95 (m, 10 H). Anal. ($C_8H_{14}O_3$): C, H.

Ethyl bicyclo[5.1.0]octane-8-carboxylate was prepared from cycloheptene and EDA (catalyst Rh-CH_3): bp 59–65 °C (0.1 mm); ratio of exo to endo = 2.4; NMR ($CDCl_3$, Me_4Si) δ 4.08 (q, J = 7 Hz, 2 H, –C(O)OCH_2), 0.9–2.46 (m, 16 H). Anal. ($C_{11}H_{18}O_2$): C, H.

Methyl *exo*-bicyclo[6.1.0]nonane-9-carboxylate was prepared from cyclooctene and MDA (catalyst Rh-CH_3): bp 80 °C (0.3 mm); IR 1730 cm^{-1} (C=O); NMR (CCl_4, HMDS) δ 3.5 (s, 3 H, CH_3 ester), 2.32–0.51 (m, 15 H). Anal. ($C_{11}H_{18}O_2$): C, H.

Cyclopropanation of Isoprene. The isomers were isolated by preparative VPC and identified by NMR ($CDCl_3$, Me_4Si) by LIS with Eu.

(a) Ethyl 2-(2-isopropenyl)cyclopropane-1-carboxylate (mixture of *E* and *Z* isomers) was prepared from isoprene and EDA (catalyst Rh-CH_3): IR 1728 (C=O), 1645 cm^{-1} (C=C); NMR δ 5.2–4.6 (m, 2 H), 4.05 and 4.0 (q, 2 H, CH_2CH_3, *E* and *Z*), 2.1–0.8 [m, 10 H, including a d at 1.66 (CH_3), a t at 1.25 (CH_2CH_3, *E*), and a t at 1.20 (CH_2CH_3, *Z*)]. Anal. ($C_9H_{14}O_2$): C, H.

(b) Ethyl (*E*)-2-vinyl-2-methylcyclopropane-1-carboxylate: IR 1730 (C=O), 1638 cm^{-1} (C=C); NMR δ 6.1–4.7 (m, 3 H), 4.08 (9, 2 H), 2.0–0.9 [m, 9 H, including a s at 1.32 (CH_3) and a t at 1.26 (CH_2CH_3)]. Anal. ($C_9H_{14}O_2$): C, H.

(c) Ethyl (*Z*)-2-vinyl-2-methylcyclopropane-1-carboxylate: IR 1730 (C=O), 1638 cm^{-1} (C=C); NMR δ 6.1–4.78 (m, 3 H), 4.05 (q, 2 H), 1.94–0.76 [m, 9 H, including a s at 1.28 (CH_3) and a t at 1.26 (CH_2CH_3)]. Anal. ($C_9H_{14}O_2$): C, H.

Cyclopropanation Products of 1,3-Pentadiene. The isomers were identified according to the data of ref 23.

Cyclopropanations of Norbornene and Norbornadiene. The isomers were identified according to ref 24.

Acknowledgment. We are indebted to the FNRS, Belgium, for a fellowship to N.P. and for a grant (high-pressure LC equipment). We also acknowledge the generous support of the Service de la Programmation de la Politique Scientifique, Bruxelles. We are grateful to Dr. Warin for recording and interpreting the NMR spectra and to Dr. Weber for mass spectral measurements.

Registry No. Methyl *cis*-2-(*p*-methoxyphenyl)cyclopropanecarboxylate, 72228-94-5; methyl *trans*-2-(*p*-methoxyphenyl)cyclopropanecarboxylate, 72228-95-6; *p*-methoxystyrene, 637-69-4; methyl *cis*-2-(*p*-methylphenyl)cyclopropanecarboxylate, 72228-96-7; methyl *trans*-2-(*p*-methylphenyl)cyclopropanecarboxylate, 72228-97-8; *p*-methylstyrene, 622-97-9; methyl *cis*-2-(*p*-chlorophenyl)cyclopropanecarboxylate, 72228-98-9; methyl *trans*-2-(*p*-chlorophenyl)-cyclopropanecarboxylate, 72228-99-0; *p*-chlorostyrene, 1073-67-2; methyl *cis*-2-(*o*-nitrophenyl)cyclopropanecarboxylate, 72229-00-6; methyl *trans*-(2-*o*-nitrophenyl)cyclopropanecarboxylate, 72229-01-7; methyl *cis*-2-(*p*-nitrophenyl)cyclopropanecarboxylate, 72229-02-8; methyl *trans*-2-(*p*-nitrophenyl)cyclopropanecarboxylate, 72229-03-9; (*o*-nitrophenyl)styrene, 579-71-5; (*p*-nitrophenyl)styrene, 100-13-0; butyl 2-decylcyclopropanecarboxylate, 72229-04-0; 1-dodecene, 112-41-4; butyl 2-acetoxycyclopropanecarboxylate, 72229-05-1; vinyl acetate, 108-05-4; ethyl *cis*-2-ethoxycyclopropanecarboxylate, 71666-09-6; ethyl *trans*-2-ethoxycyclopropanecarboxylate, 60212-44-4; ethyl vinyl ether, 109-92-2; ethyl *endo*-bicyclo[5.1.0]octane-8-carboxylate, 4729-32-2; ethyl *exo*-bicyclo[5.1.0]octane-8-carboxylate, 4729-45-7; cycloheptene, 628-92-2; methyl *exo*-bicyclo[6.1.0]nonane-9-carboxylate, 59895-61-3; cyclooctene, 931-88-4; isoprene, 78-79-5; ethyl *cis*-2-(2-isopropenyl)cyclopropane-1-carboxylate, 52390-22-4; ethyl *trans*-2-(2-isopropenyl)cyclopropane-1-carboxylate, 52345-59-2; ethyl *trans*-2-vinyl-2-methylcyclopropane-1-carboxylate, 52345-60-5; ethyl *cis*-2-vinyl-2-methylcyclopropane-1-carboxylate, 52345-63-8; 1,3-pentadiene, 504-60-9; norbornene, 498-66-8; norbornadiene, 121-46-0; styrene, 100-42-5; ethyl *trans*-2-phenylcyclopropanecarboxylate, 946-39-4; ethyl *cis*-2-phenylcyclopropanecarboxylate, 946-38-3; ethyl diazoacetate, 623-73-4; 1-hexene, 592-41-6; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; *cis*-3-hexene, 7642-09-3; *cis*-2-octene, 7642-04-8; *trans*-2-octene, 13389-42-9; *trans*-4-octene, 14850-23-8; TME, 563-79-1; cyclopentene, 142-29-0; cyclohexene, 110-83-8; indene, 95-13-6; dimethyl maleate, 624-48-6; dihydropyran, 110-87-2; 1,5-hexadiene, 592-42-7; 1,3-cyclohexadiene, 592-57-4; 1,5-cyclooctadiene, 111-78-4; MDA, 6832-16-2; BDA, 24761-88-4; methyl 2-butylcyclopropanecarboxylate, 64583-94-4; methyl 2,3-dimethylcyclopropanecarboxylate, 72258-11-8; methyl 2,3-diethylcyclopropanecarboxylate, 61452-44-6; ethyl 2,3-diethylcyclopropanecarboxylate, 61490-19-5; butyl 2,3-diethylcyclopropanecarboxylate, 61452-45-7; methyl 2-methyl-3-pentylcyclopropanecarboxylate, 61452-46-8; butyl 2-methyl-3-pentylcyclopropanecarboxylate, 61452-47-9; methyl 2,3-dipropylcyclopropanecarboxylate, 61490-20-8; butyl 2,3-dipropylcyclopropanecarboxylate, 61452-48-0; ethyl 2,2,3,3-tetramethylcyclopropanecarboxylate, 771-10-8; ethyl bicyclo[3.1.0]hexane-6-carboxylate, 72229-06-2; methyl bicyclo[4.1.0]heptane-7-carboxylate, 61452-49-1; ethyl bicyclo[4.1.0]heptane-7-

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carboxylate, 52917-64-3; butyl bicyclo[4.1.0]heptane-7-carboxylate, 61452-50-4; ethyl bicyclo[6.1.0]nonane-9-carboxylate, 72258-12-9; 4-(ethoxycarbonyl)tricyclo[4.4.0.0^{3,5}]decane, 72258-13-0; 3-(ethoxycarbonyl)tricyclo[3.2.1.0^{2,4}]octane, 72258-14-1; ethyl 2-acetoxycyclopropanecarboxylate, 72229-07-3; 7-(ethoxycarbonyl)-2-oxabicyclo[4.1.0]hexane, 72229-08-4; ethyl 2-(1-propenyl)cyclopropanecarboxylate, 16783-15-6; ethyl 2-ethenyl-3-methylcyclopropanecarboxylate, 51607-42-2; ethyl 2-ethenyl-2-methylcyclopropanecarboxylate, 21304-31-4; ethyl 2-(1-methylethenyl)cyclopropanecarboxylate, 18864-65-8; ethyl 2-(3-butenyl)cyclopropanecarboxylate, 61452-53-7; 7-(ethoxycarbonyl)bicyclo[4.1.0]hept-2-ene, 61452-52-6; 7-(ethoxycarbonyl)bicyclo[6.1.0]non-4-ene, 59891-06-4; 3-(ethoxycarbonyl)tricyclo[3.2.1.0^{2,4}]oct-6-ene, 59811-70-0; 1-octene, 111-66-0; 1-hexyne, 693-02-7; methyl 2-hexylcyclopropanecarboxylate, 72229-09-5; ethyl 2-decylcyclopropanecarboxylate, 15898-93-8; methyl 2-butyl-2-cyclopropenecarboxylate, 67500-40-7.

Study of the Electrochromism of Methoxyfluorene Compounds

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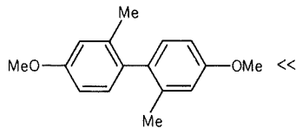
The electrochemical and electrochromic properties of a variety of polysubstituted fluorene compounds have been studied. The 2,7- and 2,3-dimethoxy-, 2,3,6,7-tetramethoxy-, and 2,3,4,5,6,7-hexamethoxyfluorenes are highly reversible electrochromic materials. One-electron oxidation of these materials yields deeply colored, stable radical cations. The structure–property relationships observed for the electrochemical and absorption behavior of these materials are discussed.

Electrochromism, a reversible optical absorption change induced in a material by an applied electric field or current, has been observed in a relatively large number of organic and inorganic substances.[1] In general, widespread applications have not been realized due to a variety of material problems, including poor electrochemical nucleic; between the colored and colorless states, low optical efficiencies, electrode incompatibilities, etc. However, increasing technological demands (e.g., low-power, nonemissive information displays) prompt the need for highly reversible, optically efficient electrochromic materials. The ultimate development of these systems will require better understanding of the relationships of molecular structure to the electrochemical and electrochromic behavior of materials. In the present study we describe these properties for a new class of organic electrochromic materials, namely, the polymethoxylated fluorenes.

In a series of papers describing the oxidation of methoxybiphenyls and related compounds,[2-5] Parker and coworkers noted the unusual stability of the corresponding radical cations and dications. They observed a direct relationship between the stability of the oxidation products and the planarity of the aromatic nuclei; e.g., the relative stabilities of the radical cations of compounds **1**–**3**, were found to be as shown. Of interest for the present study, the radical cation of the methylene-bridged biphenyl **3** was reportedly a deep blue color and displayed a half-life of approximately 6 h in nitrobenzene solution.[2] These observations prompted us to investigate further the electrochromism of bridged biphenyl compounds.

Results and Discussion

Important structures for subsequent discussion are either indicated as shown or are in Table I.



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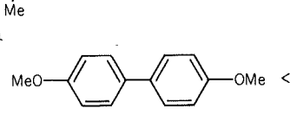

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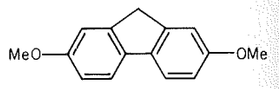

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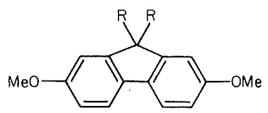
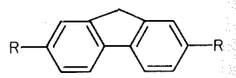
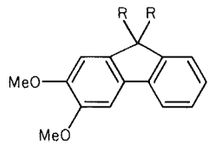


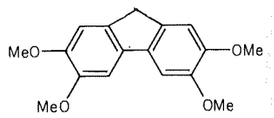
3, R = H
4, R = Me



5, R = NH_2
6, R = O_2CCH_3
7, R = OCH_2Ph



12, R = H
13, R = Me



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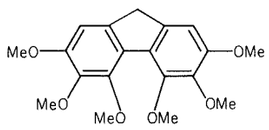

15

Cyclic Voltammetry Data. The previous reports of Parker et al.[2-5] established the ability of methoxy substituents to stabilize the oxidation products of fluorene materials. We have extended these studies to a variety of substituents and substitution patterns to determine the key structural unit(s) required for the desired electrochemical stability. Our results of cyclic voltammetric (CV) measurements for a number of substituted fluorenes are summarized in Table I. Irreversible cyclic voltammograms were observed for the parent unsubstituted fluorene as well as for the acetoxy and aza derivatives **6** and **8**, respectively. The monomethoxyfluorenes **9**–**11** also displayed irreversible oxidations, suggesting that a minimum of two such substituents are necessary for stabilization of the radical cation. The dimethoxy derivatives **3**, **4**, **12**, and **13**, the diamino derivative **5**, the bis(benzyloxy) derivative **7** and the tetra- and hexamethoxy derivatives **14** and **15** undergo reversible or quasi-reversible one-electron oxidations at a sweep rate of 200 mV/s. In several cases the peak separations for the anodic and cathodic processes ($E_{Pa}^1 - E_{Pc}^1$) deviated from the theoretical 60 mV for reversible electrochemical reaction; however, the ratio of peak currents was in all cases approximately 1. A second reversible or quasi-reversible one-electron oxidation peak was observed only for compounds **3**, **4**, **5**, **14**, and **15**. It should be noted that the reversible two-electron process could be observed for compounds **3**, **4**, **14**, and **15** only when the system was rigorously anhydrous (e.g., employing trifluoroacetic anhydride as a water scavenger).[6]

The peak potentials of the first oxidation (E_{Pa}^1) for the monomethoxy analogues **9**–**11** confirm that electron-donating substituents located ortho or para to the biphenyl linkage are more effective at reducing the oxidation potential than a meta substituent. As shown by compounds **3** and **10** the two para substituents exert a greater electron-donating influence than one (i.e., E_{Pa}^1 of 0.91 and 1.23 V, respectively). A surprisingly low E_{Pa}^1 value of 0.90 V was observed for the meta,para-substituted analogue **12**, comparable, in fact, to that observed for the para,para derivative **3** (0.91 V). The electron-donating influence is further manifested in the low oxidation potential of the tetramethoxy compound **14**. This trend is reversed, however, for the hexamethoxyfluorene **15** for which E_{Pa}^1 was approximately 110 mV higher than that for the tetramethoxy compound **14**. This may be a result of the distortion from planarity which results from steric crowding of the methoxy substituents in **15**, thus reducing their donating ability.

Table I. Voltammetric Oxidation of Substituted Fluorenes[a]

compd	E_{Pa}^1 [c]	E_{Pc}^1 [c]	E_{Pa}^2 [c]	E_{Pc}^2 [c]	ΔE, mV[d]	reversibility,[f] %
3	0.91	0.79	1.41	1.28	500	99 (30[b])
4	0.96	0.84	1.50	1.36	540	99 (70[b])
5[b]	0.43	0.37	0.72	0.65	290	92
6[b]	1.66[e]		2.14[e]			
7	1.14	1.08	1.48[e]		340	
8[g]	0.96[e]					
9[h]	1.54[e]					
10[i]	1.23[e]					
11[j]	1.34[e]					
12	0.90	0.81	1.52[e]		620	99
13	1.04	0.92	1.66[e]		620	99
14	0.76	0.65	1.25	1.15	490	99
15	0.87	0.81	1.22	1.16	350	99

[a] Unless otherwise noted 1.0 mM in CH_2Cl_2/TFAn/TFA (95:2.5:2.5) containing n-Bu_4NBF_4 (0.1 M). [b] 1.0 mM in MeCN containing n-Bu_4NBF_4 (0.1 M). [c] In volts vs. the aqueous saturated calomel electrode, measured at a sweep rate of 200 mV/s. [d] $E_{Pa}^1 = E_{Pa}^2 = \Delta E$. [e] No reverse peak. [f] $(Q_{redn}/Q_{oxidn})100$. [g] 4-Azafluorene. [h] 1-Methoxyfluorene. [i] 2-Methoxyfluorene. [j] 4-Methoxyfluorene.

Table II. Electronic Absorption Spectral Data[a]

cation radical of	λ_{max}, nm	ϵ, L cm^{-1} mol^{-1}	rel optical efficiency[c]
3	385	20 400	1
	400	31 200	
	411	40 400	
	690	16 000	
	758	20 800	
4	385	32 800	1.2
	695	18 400	
	760	24 800	
5[b]	360	16 800	
	609	11 000	
	820	13 800	
12	600	6 200	0.2
13	597	11 300	0.3
14	412	11 600	0.08
	612	3 100	
15	415	44 300	1.1
	635	20 100	
	688	28 000	
2	415	21 000	
	425	23 500	
	732	12 500	
	804	21 000	

[a] Unless otherwise indicated CH_2Cl_2:TFAn:TFA (95:2.5:2.5). [b] MeCN. [c] See text for explanation.

Coulometry Data. Having determined the cyclic voltammetric reversibilities of the polymethoxyfluorenes, we utilized coulometric measurements to study the stability of the fluorene radical cations on longer time scales. A 1 mM solution of the electrochromic material in a preelectrolyzed solvent was electrolyzed at a constant potential (120 mV more anodic than E_{Pa}^1) for a time sufficient to oxidize approximately 80% of the material. The darkly colored solution was kept for approximately 10 min and the electrolysis then reversed. Reversibility was computed as the $(Q_{redn}/Q_{oxidn})100$ averaged over repeated cycles. As indicated in Table I, reversibilities of greater than 99% were determined for the methoxy fluorene derivatives **3**, **4**, and **12**–**15** in CH_2Cl_2/trifluoroacetic anhydride/trifluoroacetic acid (95:2.5:2.5). For comparison, the well-known electrochromic material heptylviologen[1] yields electrochemical reversibilities of 80–85% (H_2O, CH_3CN) in a similar examination. A 92% reversibility was obtained for the diaminofluorene **5** measured in CH_3CN. The coulometric reversibilities measured for the methoxyfluorenes were sensitive to the presence of water. For example, a reversibility of approximately 30% was obtained for compound **3** in wet acetonitrile compared to a value of 95% obtained under anhydrous conditions. The role of the benzylic hydrogens of the fluorene nucleus in the decomposition pathways is suggested by the data for the 2,7-dimethoxyfluorene (**3**) and its 9,9-dimethyl analogue **4**. Coulometric reversibilities of approximately 30% are observed for the methylene-bridged compound **3** in wet CH_3CN compared to a value of greater than 70% for the geminally substituted derivative **4**.

Electronic Absorption Data. The electronic absorption spectral data for the radical cations of the substituted fluorenes are given in Table II. In bulk electrolysis experiments of 1 mM solutions, all of the materials display the persistent deep blue coloration of the radical cations. No change in the absorbance at λ_{max} for compounds **3**, **4**, and **12**–**15** was observed for periods of several hours. This is consistent with the radical cation stabilities determined

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