at the same temperature. After cooling, the reaction mixture was quenched by addition of methanol (12.0 ml) saturated with NH_4Cl and shaken vigorously with Zn-Cu couple[11] (3.80 g, 57.8 mg-atoms) for 20 min. The reaction mixture was diluted with methylene chloride (200 ml) and a saturated aqueous solution (100 ml) of ethylenediaminetetraacetic acid disodium salt. The insoluble materials were removed by filtration, and the filtrate was extracted twice with methylene chloride (50 and 30 ml). The combined organic layers were dried over sodium sulfate and concentrated to give an oily residue (2.16 g), whose GLC analysis showed the yield of the desired adduct 1 (retention time 8 min) to be 83%. The oil was dissolved in methylene chloride (20 ml) and added dropwise to vigorously stirred *n*-hexane (200 ml). The resulting insoluble precipitates were removed by filtration and the filter cake was washed thoroughly with *n*-hexane. The filtrate and washing were combined and evaporated to leave an oil (1.10 g), which was chromatographed on a silica gel column (15 mm diameter, 15.0 g). Elution with 1:1 benzene–*n*-hexane (110 ml) and 1:10 ethyl acetate–*n*-hexane (50 ml) and collecting 10-ml fractions gave an oily 1 (95% pure by NMR analysis, 520 mg, 66% yield) in fractions 9–15, which was identified by comparison of the NMR spectrum with the reported one.[12] Bulb-to-bulb distillation of this oil gave an analytical sample (375 mg), bp 70–120° (bath temperature) (2 mm), as colorless crystals, mp 45–48° (lit.[12] an oil).

2,2-Dimethylbicyclo[3.2.1]octan-3-one (2). Cycloadduct 1 (300 mg, 2.00 mmol) was stirred in ethyl acetate (5.0 ml) containing 10% Pd/C (30 mg) under atmospheric pressure of hydrogen at room temperature for 3 hr. The catalyst was removed by filtration and the filtrate was concentrated to give an oil (350 mg). Bulb-to-bulb distillation of the oil gave 2 (242 mg, 80% yield) as colorless crystals, bp 80–130° (bath temperature) (2 mm), mp 35–37° (lit.[3d] an oil), showing an NMR spectrum identical with the reported one.[3d] Its 2,4-dinitrophenylhydrazone melted at 117–118° (lit.[3d] mp 117.5–119.5°).

Carbocamphenilone (3). Selenium dioxide (90 mg, 0.81 mmol) and 2 (61 mg, 0.40 mmol) were mixed in dry xylene (1.2 ml) and the slurry was heated at 140° with stirring. After 4 hr the reaction mixture was subjected directly to column chromatography (8 mm diameter) on silica gel (2.0 g). The column was eluted with *n*-hexane followed by benzene. After concentration the fraction eluted with benzene yielded carbocamphenilone (3) (79 mg, quantitative yield) as yellow crystals. On recrystallization from *n*-pentane an analytical sample was obtained, mp 57–61° (lit. mp 49–52°,[2a] 59–60°,[2f] 50–53°,[3d] 58–59°,[4a] 56–59°,[4b] and 48–50°[4d]). Its ir and NMR spectra were identical with reported ones.[4d]

4,4-Dimethylbicyclo[3.2.1]oct-6-ene-2,3-dione (6,7-Dehydrocarbocamphenilone) (5). A mixture of 1 (136 mg, 0.90 mmol) and selenium dioxide (200 mg, 1.80 mmol) in dry xylene (2.5 ml) was stirred at 140° for 4 hr. The resulting mixture was chromatographed on a silica gel column (8 mm diameter, 4.0 g) with *n*-hexane (20 ml), benzene (75 ml), and 1:10 ethyl acetate–benzene (50 ml) and 5-ml fractions were collected. Fractions 14–21 gave a yellow, crystalline 5 (106 mg, 72% yield), which was recrystallized from *n*-pentane to afford an analytical specimen: mp 57–61°; ir (CCl_4) 1736 (weak) and 1720 cm^{-1} (C═O); uv-visible max (isooctane) 249 nm (ϵ 675), 294 (141), and 431 (77.7); NMR (CCl_4) δ 1.14 and 1.24 (s, 3 H each, CH_3), 2.40 (m, 2 H, CH_2), 2.58 [m, 1 H, $(CH_3)_2CCH$], 3.42 (m, 1 H, COCH), 5.97 (dd, 1 H, J = 2.3 and 6.0 Hz, $(CH_3)_2CCHCH$═), and 6.54 (dd, 1 H, J = 2.3 and 6.0 Hz, COCHCH═). The assignment of NMR signals was confirmed by double-resonance technique; irradiation at δ 3.42 changed the δ 5.97 signal into a doublet with J = 6.0 Hz, and irradiation at δ 2.58 gave a doublet with J = 6.0 Hz at δ 6.54.

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 73.11; H, 7.37.

Registry No.—1, 22940-29-0; 2, 55682-09-2; 3, 27455-93-2; 5, 55682-10-5; cyclopentadiene, 542-92-7; 1,1,3-tribromo-3-methylbutan-2-one, 1578-05-8.

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Regioselectivity in the Reaction of $C_5H_5Fe(CO)_2(isobutylene)^+BF_4^-$ with Polyenes

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The recently demonstrated abilities of the $C_5H_5Fe(CO)_2^+(Fp^+)$ group to activate olefins toward nucleophilic attack[1] and to stabilize highly reactive alkenes (e.g., cyclobutadiene[2] and benzocyclobutadiene[3]) promise to be of considerable synthetic value. In connection with our evaluation of this organometallic moiety as a protecting group for the carbon–carbon double bond,[4] we have investigated the regioselectivity for the metalation of unsymmetrical polyenes with $Fp(isobutylene)^+BF_4^-$ (1).[5]

When 1,2-dichloroethane solutions of 1 were heated (65–70°, 10 min) in the presence of a tenfold excess of the polyenes 4-vinylcyclohexene (2), *trans*-piperylene (3), 2-methyl-1,5-hexadiene (4), 1-octen-4-yne (5), *endo*-dicyclopentadiene (6), 1,3,6-heptatriene (7), and 5-vinyl-2-norbornene (8), 1:1 complexes formed as air-stable yellow solids in good yield.[6] The structures of the complexes 9–15 followed readily from their ^1H NMR spectra (Table I) since olefinic proton absorptions are generally shielded ca. 1.0–1.7 ppm upon coordination by Fp^+ whereas allylic proton absorptions are correspondingly deshielded ca. 0.4 ppm. For each substrate (except 8) only one positionally isomeric complex was detectable by NMR, indicating at least 90–95% regioselectivity. Additional support for the assigned structures was obtained by comparison of ^1H NMR spectra with model systems or by hydrogenation of the free unsaturation and comparison of the resulting complexes with authentic samples.[7]

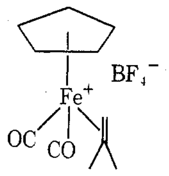

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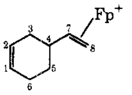
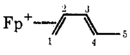
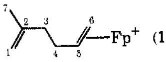
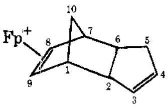
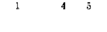
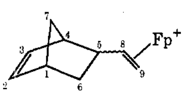
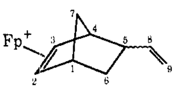
Table I
Regioselectivity for $C_5H_5Fe(CO)_2(isobutylene)^+BF_4^-$ + Polyene ⟶ $C_5H_5Fe(CO)_2(polyene)^+BF_4^-$ + Isobutylene

Polyene	Complex	Yield, %[a]	NMR spectrum, δ (ppm)[b]
2	 (9)	76	5.7 (s, Cp, $H_{1,2}$), 5.0 (m, H_7), 3.9 (d, 9 Hz, H_{8cis}), 3.5 (dd, 15 Hz, H_{8trans}), 2.8–1.4 (bm, $H_{3,4,5,6}$)
3	 (10)	83	6.6 (m, H_3), 5.9 (m, H_4), 5.6 (s, Cp), 5.4 (m, H_2), 3.7 (d, 7 Hz, H_{1cis}), 3.5 (d, 14 Hz, H_{1trans}), 1.9 (d, 6 Hz, H_5)
4	 (11)	58	5.6 (s, Cp), 5.2 (m, H_5), 4.8 (bs, H_1), 4.0 (d, 8 Hz, H_{6cis}), 3.5 (d, 15 Hz, H_{6trans}), 2.4 (m, $H_{3,4}$), 1.8 (bs, H_7)
5	 (12)	65	5.9 (s, Cp), 5.3 (m, H_2), 3.6 (d, 9 Hz, H_{1cis}), 3.4 (d, 18 Hz, H_{1trans}), 2.9 (t, $J = 8$ Hz, H_3), 2.0–1.2 (m, $H_{6,7}$), 1.0 (t, 6 Hz, H_8)
6	 (13)	85	5.6 (s, Cp, $H_{8,9}$), 5.3 (bm, $H_{3,4}$), 3.4 (bm, H_2), 3.0 (bm, $H_{1,6,7}$), 2.3 (bm, H_5), 1.0 (d, 12 Hz, H_{10}), −0.1 (d, 12 Hz, H_{10})
7[c]	 (14)[c]	58	6.7 (m, $H_{3,4}$), 5.9 (s, Cp), 5.8 (s, Cp), 5.8 (bm, $H_{2,6}$), 5.2 (bd, 6 Hz, H_{7cis}), 5.1 (bd, 13 Hz, H_{7trans}), 4.2 (d, 9 Hz, H_{1cis}), 3.9 (d, 8 Hz, H_{1cis}), 3.7 (d, 13 Hz, H_{1trans}), 3.6 (d, 14 Hz, H_{1trans}), 3.0 (bt, 7 Hz, H_5)
8[d]	 (15a)[d] ca. 65:35	65	6.2 (bm, $H_{2,3}$), 5.55 (s, Cp), 4.9 (m, H_8), 3.5 (m, H_9), 2.9 (bs, $H_{1,4,5}$), 2.5–0.9 (bm, $H_{6,7}$)
	 (15b)[d]		5.6 (s, Cp), 5.2 (m, $H_{2,3,8}$), 4.9 (bd, H_9), 2.9 (bs, $H_{1,4,5}$), ~2.2 (bm, H_6), 0.9 (bd, ~12 Hz, H_7) −0.1 (bd, ~12 Hz, H_7)

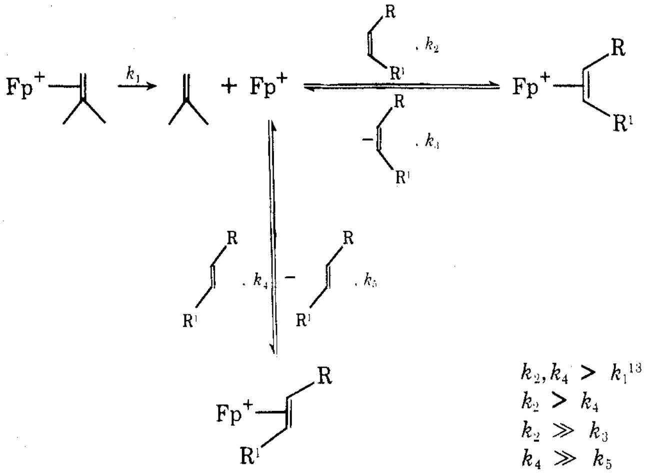
[a] No attempts were made to optimize yields. [b] Spectra of 9, 10, 11, 13, 15a, and 15b obtained in CD_3NO_2 solution; CD_3COCD_3 was the solvent for 12 and 14. [c] Mixture of cis and trans isomers. [d] Mixture of exo and endo vinyl derivatives. Complexes 15a and 15b were not separated but characteristic ^1H resonances for each were discernible in the spectrum of the mixture.

The observed regioselectivity for the exchange process generally parallels the stability trends of transition metal–alkene complexes.[8] It is thus possible to rationalize formation of **9**, **10** and **11** in terms of steric effects and of **13** on the basis of relief of strain.[9,10] Preferential coordination to the double bond of enyne **5** is not surprising in view of the apparent instability of Fp(alkyne)$^+$ salts.[11] The regiospecific formation of **14** is particularly noteworthy since, although dienes are generally more reactive toward electrophilic reagents, stability constants for Ag(I)-conjugated diene complexes are somewhat lower than for simple alkene complexes.[12]

While these products are probably the thermodynamically more stable, the exchange process appears to be kinetically controlled and essentially irreversible as indicated by the following experiments. ^1H NMR analysis of aliquots removed after 2, 5, 8, 12, and 15 min during the reaction of **1** with 10 equiv of a 1:1 mixture of *cis*- and *trans*-2-octene showed the ratio of cis/trans complexes (**17**, **18**), 2.5:1, to be essentially constant throughout the reaction period. Furthermore, when Fp(*trans*-2-octene)$^+BF_4^-$ (**18**) was heated (65°, 10 min) with 10 equiv of *cis*-2-octene, the recovered Fp(2-octene)$^+BF_4^-$ (30%) was mostly trans (ca. 67%). These results are consistent with the mechanism outlined in Scheme I.

Preferential binding of the Fp$^+$ moiety to less substituted or more strained double bonds and to conjugated diene units should allow activation of a single position in a polyene toward nucleophilic attack. This regioselectivity also provides a method for protection of the same double bonds during hydrogenations and electrophilic and certain other addition reactions.[4] We are currently exploring the above applications.

Scheme I



Experimental Section

NMR spectra were recorded on a Perkin-Elmer R-24 spectrometer with Me_4Si as internal standard. Ir spectra were obtained on a Beckman IR 10 spectrometer. The polyenes **2**–**8** and *cis*- and *trans*-2-octene were obtained commercially and used without further purification. The complex **1** was prepared according to the method of Giering and Rosenblum.[5]

Preparation of $C_5H_5Fe(CO)_2(h^2\text{-polyene})^+BF_4$ Complexes (9–15). The general procedure is as described by Giering and Rosenblum.[5] The olefin (30 mmol), **1** (3.0 mmol), and 40 ml of 1,2-dichloroethane were placed in an erlenmeyer flask. A rubber septum fitted with a syringe needle and thermometer was secured to the flask and the mixture was heated at 65–70° for 10–15 min. After cooling to room temperature and filtering to remove any $C_5H_5Fe(CO)_3^+BF_4^-$, the solvent and excess polyene were removed by evaporation under reduced pressure. The residue was dissolved in a minimum of acetone or nitromethane and filtered, and the filtrate was added dropwise to a large volume (100–200 ml) of ether with scratching to afford the complexes as yellow, air-stable precipitates. Purification was accomplished by reprecipitation from nitromethane–ether or acetone–ether.

Complex **7** was conveniently separated from a small amount (12%) of 1-6 bis-Fp$^+$ complex **16** by trituration of the reaction residue with several small portions of CH_2Cl_2. This bis complex was identified by its NMR spectrum (CD_3NO_2): δ 6.4–7.0 (m, 2 H, olefinic), 5.7 (s, 5 H, Cp), 5.6 (s, 5 H, Cp), 4.8–5.5 (m, 2 H, coordinated $CH{=}CH_2$), 3.5–4.2 (m, 4 H, coordinated $CH{=}CH_2$), 2.5 (bm, 2 H, allylic).

All new complexes exhibited prominent infrared absorptions (CH_3COCH_3) at 2055, 2020 (M–C≡O), and 1025 cm^{-1} (BF_4^-). NMR spectral data are presented in Table I. Satisfactory C and H analyses were obtained for all new compounds except **11** and **15**.

Hydrogenation of Fp(vinylcyclohexene)$^+$BF$_4^-$ (9). Complex **9** (0.186 g, 0.50 mol), 10 mg of 5% Pd/C, and 5 ml of trifluoroacetic acid were stirred at 25° under 1 atm of hydrogen until gas uptake ceased (ca. 15 min). The catalyst was removed by filtration and the filtrate was added dropwise to 100 ml of ether. The NMR spectrum of the resulting yellow precipitate (0.140 g, 75%) was identical with that produced from the reaction of **1** with vinylcyclohexane: δ (CD_3NO_2) 5.7 (s, 5 H, Cp), 5.1 (m, 1 H, $CH{=}CH_2$), 3.8 (d, J = 9 Hz, 1 H, $CH{=}CH_2$ cis), 3.5 (d, J = 16 Hz, 1 H, $CH{=}CH_2$ trans), 1.0–2.2 (6 m, 1 H, ring H).

Anal. Calcd for $C_{15}H_{19}BF_4FeO_2$: C, 48.18; H, 5.12. Found: C, 48.11; H, 5.09.

Fp(*cis*-2-octene)$^+$BF$_4^-$ (17). The reaction of **1** with *cis*-2-octene according to the general method (above) gave **17** (68%): NMR (acetone-d_6) δ 5.80 (s, 5 H, Cp), 5.3 (bm, 2 H, complexed $CH{=}CH$), 2.5–0.8 (bm, 14 H, CH_2, CH_3).

Anal. Calcd for $C_{15}H_{21}BF_4FeO_2$: C, 47.91; H, 5.64. Found: C, 47.89; H, 5.48.

$C_5H_5Fe(CO)_2$(*h*^{2}-*trans*-2-octene)$^+$BF$_4^-$ (18). *trans*-2-Octene and **1** gave **18** (66%); NMR (acetone-d_6) δ 5.85 (s, 5 H, Cp), 4.9 (bm, 2 H, complexed $CH{=}CH$), 2.5–0.7 (bm, 14 H, CH_2, CH_3).

Anal. Calcd for $C_{15}H_{21}BF_4FeO_2$: C, 47.91; H, 5.64. Found: C, 47.75; H, 5.46.

Monitored Competitive Reaction of 1 with *cis*- and *trans*-2-Octene. *cis*-2-Octene (30 mmol), *trans*-2-octene (30 mmol), **1** (6 mmol), and 60 ml of dichloroethane were heated in the usual fashion. Aliquots (10 ml) were withdrawn by syringe after 2.5, 5, 8, 12, and 15 min once the temperature reached 55° and transferred to separate flasks. The individual aliquots were filtered, the filtrates were added to ether, and the resulting precipitates were analyzed by NMR. Integration of the complexed olefinic proton absorptions indicated that the ratio of cis/trans complex, 2.5:1, was unchanged during the course of the reaction.

Reaction of $C_5H_5Fe(CO)_2$(*trans*-2-octene)$^+$BF$_4^-$ (18) with *cis*-2-Octene. *cis*-2-Octene (5.3 mmol), **18** (0.53 mmol), and 40 ml of dichloroethane were heated at 65–70° for 10 min and allowed to cool. The reaction mixture was filtered and the filtrate was added to 200 ml of ether. The resulting yellow precipitate (0.06 g, 30%) was found by NMR to be composed to ca. 67% trans complex **18** and 33% cis complex **17**.

Acknowledgment. The authors thank Professor M. Rosenblum for helpful discussions. Financial support provided by Boston College is also gratefully acknowledged.

Registry No.—**1**, 41707-16-8; **2**, 100-40-3; **3**, 2004-70-8; **4**, 4049-81-4; **5**, 24612-83-7; **6**, 1755-01-7; *cis*-**7**, 55758-72-0; *trans*-**7**, 44607-51-4; *exo*-**8**, 23890-32-6; *endo*-**8**, 25093-48-5; **9**, 55758-75-3; **10**, 55758-77-5; **11**, 55822-54-3; **12**, 55758-79-7; **13**, 55758-81-1; *cis*-**14**, 55758-83-3; *trans*-**14**, 55820-95-6; *exo*-**15a**, 55758-85-5; *endo*-**15a**, 55820-97-8; *exo*-**15b**, 55758-87-7; *endo*-**15b**, 55820-99-0; *cis*-**16**, 55758-89-9; *trans*-**16**, 55821-01-7; **17**, 55758-91-3; **18**, 55821-03-9; Fp(vinylcyclohexane)$^+$BF$_4^-$, 55758-93-5; *cis*-2-octene, 7642-04-8; *trans*-2-octene, 13389-42-9.

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(6) From triene **7** a 1,6-bis-Fp$^+$ complex (**16**) also formed (12%).

(7) For example, the protons syn and anti to Fp$^+$ in **13** absorb at δ −0.2 (d, J = 12 Hz) and 0.7 (d, J = 12 Hz) while the corresponding proton absorptions for Fp (*h*^{2}-norbornadiene)$^+$BF$_4^{-5}$ are at δ −0.1 (d, J = 12 Hz) and 1.0 (d, J = 12 Hz) (ref 8). Also, hydrogenation of **9** (19% Pd/C, TFA solvent) gave Fp(vinylcyclohexane)$^+$BF$_4^-$ which had a ^{1}H NMR spectrum identical with that prepared from Fp(isobutylene)$^+$BF$_4$ and vinylcyclohexane.

(8) F. R. Hartley, *Chem. Rev.*, **73**, 163 (1973).

(9) Coordination at the 8,9 position of *endo*-dicyclopentadiene by Au(I) and Cu(I) has also been reported: R. Huttel, R. Reinheimer, and H. Dietl, *Chem. Ber.*, **99**, 462 (1966); R. G. Salomon and J. K. Kochi, *J. Am. Chem. Soc.*, **95**, 1889 (1973). Additionally, Ni-catalyzed hydrogenation of **6** proceeds selectively at the 8,9 position: C. A. Brown and V. K. Ahuja, *J. Org. Chem.*, **38**, 2226 (1973).

(10) Since back-bonding in the Fp(olefin)$^+$ complexes may not be extensive, coordination at the 8,9 position of dicyclopentadiene could be due to stronger forward (olefin–metal) donation. Since the energy of $\pi_{8,9}$ is higher than that of $\pi_{3,4}$, $\pi_{8,9}$ would interact with relatively high energy empty metal orbitals to form a lower energy bonding MO.

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(13) Preliminary results indicate that the exchange reaction is first order in **1** and zero order in alkene: M. Rosenblum and N. Genco, personal communication.

Some Observations on the Interaction of Diarylamines and Arsenic Trichloride[1]

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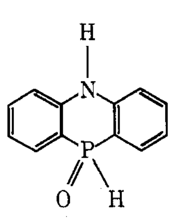
The reaction of diarylamines with phosphorus trichloride followed by treatment of the reaction mixtures with water has been found[2] to yield not only the expected heterocyclic phosphine oxides (i.e., **1** and its ring-substituted derivatives) but also the spirophosphonium chloride **2** and its derivatives. It seemed of interest to determine whether the analogous spiroarsonium chlorides could be obtained via the interaction of diarylamines and arsenic trichloride. Wieland and Rheinheimer[3] reported in 1921 that the chloroarsine **3** (now often known as Adamsite) is formed in high yield by refluxing a mixture of diphenylamine and arsenic trichloride for about 4 hr; and various ring-substituted derivatives of **3** have been prepared in a similar manner by a



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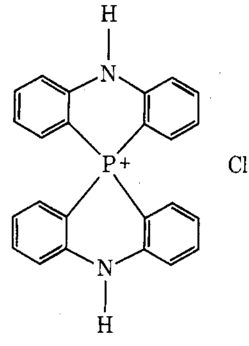

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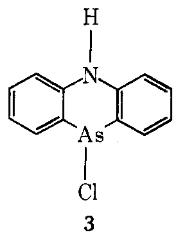

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