$S = {}^5/_2$ impurity determined from data in the range 1.7-50 K. In CD_3CN solution at room temperature[22] an upper bound for the magnetic moment of 1.5 μ_B agrees well with that in the solid state of 1.59 μ_B. It is clear from Table I that the antiferromagnetic coupling is independent of the Fe-O separation and the Fe-O-Fe angle—the latter has been noted previously.[16] Stronger coupling is observed for multiply bridged species (e.g., the symmetrical $[(Bpz_3)Fe(CH_3COO)_2(O)Fe(Bpz_3)]$ complex[7a] and unsymmetrical methemerythrin[4e]), unsymmetrical species (this work and metHr[4e]), and, possibly, heme species with linear FeOFe groups.[8] The magnetic properties of the isosceles (μ_3-oxo)triiron(III) cluster are different from those of the more symmetrical clusters.[12] Weaker coupling is observed for oxyHr.[4e] Earlier theoretical work[23] offers few clues for consequences of asymmetry.

We intend examining in detail the proton NMR of this complex, which is the first (μ-oxo)diiron(III) complex with an imidazole-derived ligand, for comparison and amplification of the corresponding data for hemerythrin.[24] We are attempting to isolate the one-electron reduced, mixed-valence compound that we observe formed in a quasi-reversible manner under cyclic voltammetry[20] and to substitute other ligands at the tetrahedral site.

Acknowledgment. The partial support of the Research Corporation and of the NIH-BRSG is gratefully acknowledged.

Registry No. $[N_5Fe\text{-}O\text{-}FeCl_3]Cl\cdot 2C_2H_5OH$, 99688-36-5.

Supplementary Material Available: Tables of positional and thermal parameters and a table of structure factor amplitudes $10|F_c|$ vs. $10|F_o|$ (27 pages). Ordering information is given on any current masthead page.

(22) Evans, D. F. *J. Chem. Soc.* **1959**, 2003-2005.
(23) (a) Kahn, O.; Briat, B. *J. Chem. Soc., Faraday Trans 2* **1976**, *72*, 1441-1446. (b) Hay, P. J.; Thibeault, J. C.; Hoffman, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884-4899. (c) Dunitz, J. D.; Orgel, L. E. *J. Chem. Soc.* **1953**, 2594-2596.
(24) (a) Maroney, M. J.; Lauffer, R. B.; Que, L., Jr.; Kurtz, D. M., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 6445-6446. (b) York, J. L.; Millett, F. S.; Minor, L. B. *Biochemistry* **1980**, *19*, 2583-2588.

Haptotropic Rearrangements in Naphthalene-Chromium Tricarbonyl Complexes

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Received November 18, 1985

One type of haptotropic rearrangement under recent study involves the migration of a coordinated metal between the different rings in a polycyclic hydrocarbon. The most extensive experimental studies in this area have been on chromium[1] and manganese[2] complexes of fluorenyl and indenyl anions, in which metal migration occurs between five- and six-membered rings (i.e., $\eta^6 \rightleftarrows \eta^5$). Similar processes have also been reported for chromium complexes of related ligands including substituted fluorenyl, 2- and 4-azafluorenyl, and fluoradenyl anions.[3] The $\eta^6 \rightleftarrows \eta^5$ migration processes also accompany certain protonations.[4] There is considerable evidence that a haptotropic migration between the two six-membered ring complexes in naphthalene or substituted naphthalenes occurs,[5] but as yet no quantitative experimental studies on such systems have been reported. Such studies would be attractive since naphthalene will probably be regarded as the simplest and most common example of a polycyclic hydrocarbon amenable to ligation.

A recent theoretical study on haptotropic processes has served to focus interest in this area.[6]

We have obtained kinetic data and calculated the activation energies for two complexes, (3-deuterio-2,7-dimethoxynaphthalene)chromium tricarbonyl, Ia, and (3-deuterio-2,6-dimethoxynaphthalene)chromium tricarbonyl, IIa. The undeuterated precursors to these species, I and II, are prepared by reaction of $Cr(CO)_6$ and the arene using standard techniques.[7,8]

Table I. Rate Constants vs. Temperature for the Haptotropic Migration of the $Cr(CO)_3$ Group in I and II[a]

temp, K	$k \times 10^5$, s^{-1} Ia $\rightleftarrows$ Ib	$k \times 10^5$, s^{-1} II $\rightleftarrows$ IIb
305	0.28 ± 0.03	
314	1.0 ± 0.2	0.072 ± 0.042
323	3.3 ± 0.3	0.31 ± 0.06
335	15 ± 3	1.1 ± 0.4
343		4.4 ± 0.3
$\Delta G^{\ddagger}$	26.8 ± 1.4 kcal/mol	28.4 ± 2.2 kcal/mol
$\Delta H^{\ddagger}$	27.2 ± 1.4 kcal/mol	28.9 ± 2.2 kcal/mol
$\Delta S^{\ddagger}$	1.3 ± 0.1 cal/(mol deg)	1.4 ± 0.1 cal/(mol deg)

[a] Each value represents the average of results from three different experiments. Rate constants were calculated from the following mechanistic scheme by standard methods: $A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$

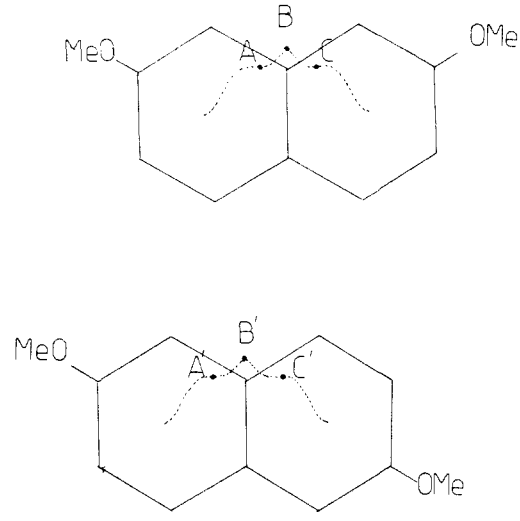

Figure 1. Pathways for haptotropic migration of the chromium carbonyl tricarbonyl group in I and II (proposed by theory, see ref 6).

(1) (a) Nicholas, K. M.; Kerber, K. C.; Stiefel, E. I. *Inorg. Chem.* **1971**, *10*, 1519-1521. (b) Nesmeyanov, A. N.; Ustynyuk, N. A.; Makarova, L. G.; Andre, S.; Ustynyuk, Yu. A.; Novikova, L. N.; Luzikov, Yu. N. *J. Organomet. Chem.* **1978**, *154*, 45-63. (c) Nesmeyanov, A. N.; Oprunenko, Yu. F.; Ustynyuk, N. A.; Lokshin, B. V.; Ustynyuk, Yu. A. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1979**, *28*, 1942-1946; *Engl. Transl.* 1799-1802. (d) Nesmeyanov, A. N.; Ustynyuk, N. A.; Novikova, L. N.; Rybina, T. N.; Ustynyuk, Yu. A.; Oprunenko, Yu. F.; Trifonova, O. I. *J. Organomet. Chem.* **1980**, *184*, 63-75. (e) Ustynyuk, N. A.; Lokshin, B. V.; Oprunenko, Yu. F.; Rosnyatovsky, V. A.; Luzikov, Yu. N.; Ustynyuk, Yu. A. *J. Organomet. Chem.* **1980**, *202*, 279-289. (f) Ceccon, A.; Gamboro, A.; Agostini, G.; Venzo, A. *J. Organomet. Chem.* **1981**, *217*, 79-89. (g) Ustynyuk, N. A.; Novikova, L. N.; Oprunenko, Yu. F.; Malyuygina, S. G. *J. Organomet. Chem.* **1984**, *277*, 75-84.
(2) (a) Rerek, M. E.; Basolo, F. *Organometallics* **1984**, *3*, 647-649. (b) Treichel, P. M.; Johnson, J. W. *Inorg. Chem.* **1977**, *16*, 749-752. (c) Treichel, P. M.; Fivizzani, K. P.; Haller, K. J. *Organometallics* **1982**, *1*, 931-934.
(3) (a) Ustynyuk, N. A.; Oprunenko, Yu. F.; Malyugina, S. G.; Trifonova, O. I.; Ustynyuk, Yu. A. *J. Organomet. Chem.* **1984**, *270*, 185-199. (b) Thoma, T.; Pleshankov, V. G.; Prostakov, N. S.; Ustynyuk, Yu. A.; Nesmeyanov, A. N.; Ustynyuk, N. A. *J. Organomet. Chem.* **1980**, *192*, 359-365.
(4) (a) Treichel, P. M.; Johnson, J. W. *J. Organomet. Chem.* **1975**, *88*, 207-214. (b) Yezernitskaya, M. G.; Lokshin, B. V.; Zdanovich, V. I.; Lobanova, I. A.; Kolobova, N. E. *J. Organomet. Chem.* **1982**, *234*, 329-335; **1985**, *282*, 363-368.
(5) (a) Deubzer, B.; Fritz, H. P.; Kreiter, C. G.; Ofele, K. *J. Organomet. Chem.* **1967**, *7*, 289-299. (b) Dotz, K. H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 644-645. (c) Greenwood, , J. M.; Veening, H.; Willeford, B. R. *J. Organomet. Chem.* **1972**, *38*, 345-348. (d) Dotz, K. H.; Dietz, R. *Chem. Ber.* **1977**, *110*, 1555-1563; **1978**, *111*, 2517-2526.
(6) Albright, T. A.; Hofmann, P.; Hoffmann, R.; Lillya, C. P.; Dobosh, P. A. *J. Am. Chem. Soc.* **1983**, *105*, 3396-3411.

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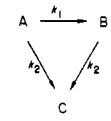
Table II. Rate Constants vs. Temperature for the Haptotropic Migration of the $Cr(CO)_3$ Group in Complexes of Several Methylnaphthalenes[a]

temp, K	$Cr(CO)_3(\eta$-1-$MeC_{10}H_7)$ $k \times 10^5$, s^{-1}	$Cr(CO)_3(\eta$-2-$MeC_{10}H_7)$ $k \times 10^5$, s^{-1}	$Cr(CO)_3(\eta$-2,3-$Me_2C_{10}H_6)$ $k \times 10^5$, s^{-1}
344		0.11	0.05
354	0.14	0.65	0.18
366	1.0	2.2	2.2
373	1.7	4.3	
383			14
H	33.7 ± 6.8 kcal/mol	30.6 ± 2.5 kcal/mol	30.9 ± 3.8 kcal/mol
S	2.6 ± 0.1 cal/(mol deg)	−0.6 ± 0.1 cal/(mol deg)	−0.9 ± 0.01 cal/(mol deg)

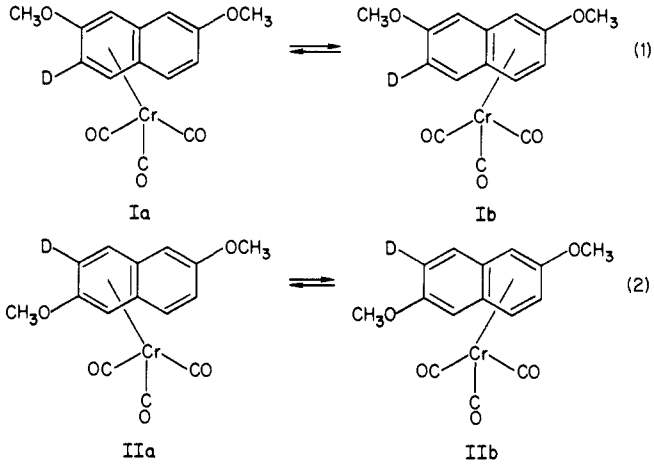
[a] Calculate assuming first order kinetics for each step in the scheme



in which A and B are the isomeric naphthalene complexes and C is the $Cr(CO)_3(\eta^6$-$C_6H_5Me)$. For this scheme the equation $\ln(1 + B/A) = k_1 t$ is applicable.

Deuteration is then accomplished by a two-step sequence involving initial lithiation by lithium diisopropylamide at −78 °C, followed by D_2O addition; this route is complete and specific (although accompanied by substantial decomposition). The position of deuterium in Ia and IIa is established from ^1H NMR data.[8]

When dissolved in benzene-d_6, both Ia and IIb are found to undergo a haptotropic migration of the metal tricarbonyl group to the undeuterated ring, with equilibrium (1:1) mixtures of Ia ⇄ Ib (eq 1) and IIa ⇄ IIb (eq 2) eventually being obtained.



Neither decomposition nor arene exchange with solvent appears to be a significant factor in these systems. It is possible to follow these processes by ^1H NMR. For the reaction Ia ⇄ Ib, the appearance and growth in intensity of a new resonance at δ 5.31 is concurrent with a decrease in intensity of the resonance at δ 6.62. Similarly for the reaction IIa ⇄ IIb, the intensity of the resonance at δ 5.01 increases while the intensity of the δ 6.78 resonance decreases. First-order rate constants for these processes at several temperatures are given in Table I; from these data, activation energies were calculated for Ia ⇄ Ib ($\Delta H^\ddagger$ = 27.2 ± 1.4 Kcal/mol) and for IIa ⇄ IIb ($\Delta H^\ddagger$ = 28.4 ± 2.2 Kcal/mol). A predictably small value for $\Delta S^\ddagger$ was also obtained for these processes.

We have obtained data for haptotropic migrations using several methyl-substituted naphthalene–chromium tricarbonyl complexes (Table II). Mixtures of isomeric complexes are formed from reactions between the hydrocarbon and $Cr(CO)_6$;[5a-c] it is possible, however, to obtain samples enriched in one of the two isomeric complexes by fractional crystallization.[5c] The conversion of such species to the second isomer in toluene-d_8 can also be followed by ^1H NMR. The duration of these studies, however, are generally limited to a fraction of one half-life due to rapid concurrent formation of $Cr(CO)_3(\eta$-$C_6D_5CD_3)$ and the naphthalene. Activation energy parameters for the three examples cited are in the range 31–34 Kcal/mol. The two isomers of these methylnaphthalenes are not equivalent, though the energy difference between isomers must be small. We do not know with certainty which isomer is more stable; consequently we do not know whether the indicated process is for conversion of the less stable isomer to more stable isomer, or vice versa. This problem does not arise in symmetric naphthalene complexes such as I and II.

The values of $\Delta H^\ddagger$ (and $\Delta S^\ddagger$) for systems I and II compare quite favorably with the parameters obtained in the $\eta^6 \rightarrow \eta^5$ haptotropic migration in several fluorenylmanganese species.[2a] They are also very close to the values predicted by theory for $Cr(CO)_3(\eta$-$C_{10}H_8)$. Values of $\Delta H^\ddagger$ for methyl-substituted naphthalene–chromium tricarbonyl species are a little higher than this, but there are also features of the study which comprise the accuracy of these values.

The rate constants for Ia ⇄ Ib are about 14 times greater than the values for IIa ⇄ IIb. One would not expect a substantial ground state energy difference in I and II, but there should be a difference in transition states in these haptotropic processes, assuming the pathway for metal migration proposed in the theoretical study. This process guides the metal along the course shown in Figure 1 with energy maxima at points A and C separated by a shallow minimum at B. In I, A and C must be identical; but in II this cannot be the case. The implication is that the methoxy groups play a small role in stabilization of the transition state which translates to a higher rate of exchange. The difference in $\Delta H^\ddagger$ corresponding to such a rate difference would be small, however; our data on $\Delta H^\ddagger$ values are not sufficiently accurate to distinguish this.

An important fact still lacking an explanation in these experiments is the lack of concurrent decomposition (or arene exchange with solvent) of Ia and IIa during these haptotropic processes. Indeed we note that literature data[9] would suggest that a methoxy

(7) Nicholls, B.; Whiting, M. C. *J. Chem. Soc.* **1959**, 551–556.

(8) I. Prepared in 8% yield by heating the reactants in dioxane at reflux for 48 h; purification was accomplished by sublimation of the excess ligand at 70–75 °C under vacuum and crystallization of the unsublimed material from $CHCl_3$/hexane. mp 134–137d. Characterized by mass spectrometric peak match: found, 324.0090; calcd 342.0086; ν(CO) (in $CDCl_3$) at 1962, 1887, 1874 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.81 s, 3.85 s (CH_3O); 5.76 d, J_{1-3} = 2.0 Hz, (H_1) δ 5.31 d of d J_{1-3} = 2.0, J_{3-4} = 7.1 Hz (H_3), 6.23 d, J = 7.1 Hz (H_4) 7.41 d, J = 9.2 Hz (H_5), 6.92 d of d, J_{5-8} = 2.1, J_{5-6} = 9.2 Hz (H) and 6.58 d, J_{5-8} = 2.1 Hz (H_8). In deuterated Ia, the 5.31 resonance is absent and the 6.23 resonance is a singlet. II. Prepared in 7% yield by heating the reactants in dioxane at reflux for 48 h; purification in a manner similar to I, mp 126–128 °C. Characterized by mass spectrometric peak match: found, 324.0081; calcd, 324.0086; ν(CO) (CH_2Cl_2) 1962, 1881, 1810 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.78, 3.82 ppm (s, 6 H, CH_3O), 551 d (J_{3-4} = 6.9 Hz) H-3), 5.76 s (H_1), 6.16 d (J_{3-4} = 6.9 Hz), 6.63 s (H_5), 7.06 d of d (J_{7-8} = 9.0, J_{5-7} = 1.5 Hz), 7.43 d (J_{7-8} = 9.0 Hz). In deuterated IIa, the 5.51 resonance is absent and the 6.16 resonance is a singlet.

(9) Mehaffey, C. A. L.; Pauson, P. L. *J. Chem. Res. Miniprint*, **1979**, 1752–1775.

group would weaken a metal–arene bond, which should if anything lead to a more facile decomposition.

Acknowledgment. This paper is based upon work supported by the National Science Foundation under Grant CHE-8210497.

Synthesis of (±)-$\Delta^{(9,12)}$-Capnellene Using Titanium Reagents

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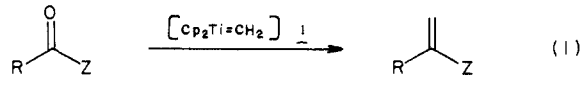
Received November 1, 1985

Titanaethylene **1** reacts with organic carbonyls and with olefins. The dominant reaction with carbonyls is "Wittig" methylenation (eq 1),[1] whereas olefins react to form metallacycles **2**[2] that can



(1)

Z = H, R', OR', NR'_2, NR'COR''

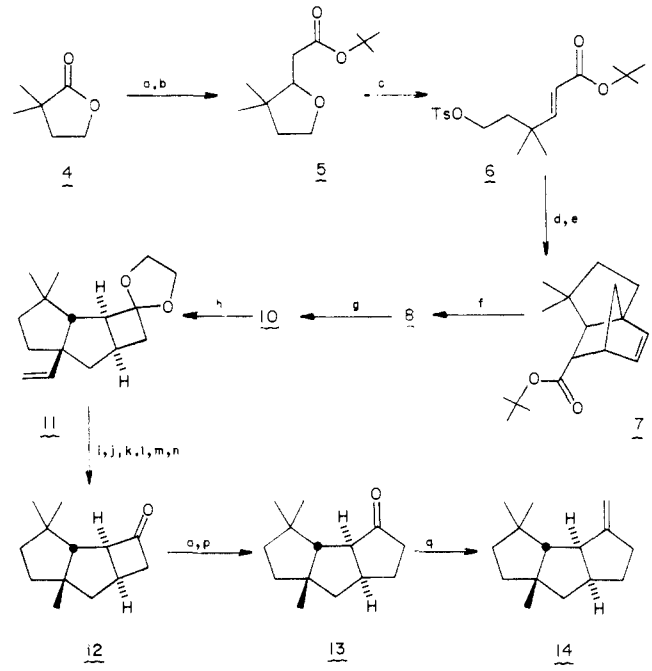
Cp = η^5-cyclopentadienyl

be used as catalysts in olefin metathesis.[3] The use of the "Tebbe Reagent" (**3**)[4] as a source of the titanaethylene fragment has

2 **3**

already found several applications in synthetic transformations and the synthesis of natural products.[1c,5] New applications are developing in polymer synthesis. Strained rings can be ring-open polymerized by using **1** as a catalyst.[6] These reactions proceed through the substituted alkylidene resulting from productive cleavage of the intermediate metallacyclobutane.[7] A molecular rearrangement that takes advantage of these two types of reactivity has been investigated and has been demonstrated to be an efficient route to $\Delta^{(9,12)}$-capnellene (**14**, Scheme I).[8] Capnellene is the presumed biosynthetic precursor to the capnellane family of nonisoprenoid sesquiterpenes. This natural product has received significant synthetic attention due to the challenging cis-anti-cis tricyclo(6.3.0.$0^{2,6}$)undecane skeletal framework. Although the details of the biological function of the capnellanes are not known,

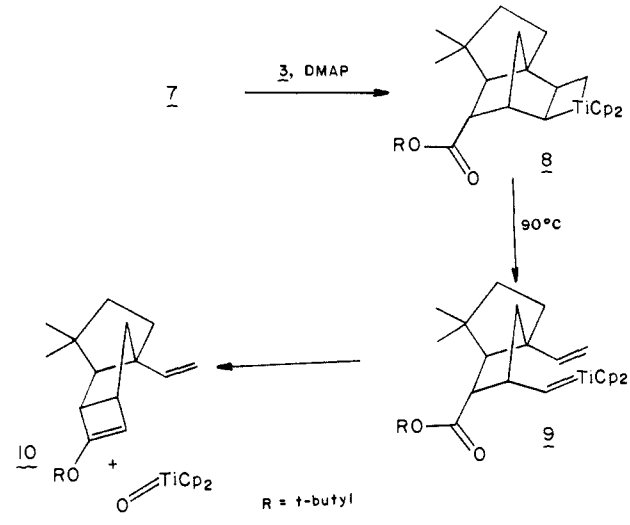
Scheme I[a]



4 **5** **6** **7** **8** **10** **11** **12** **13** **14**

[a] (a) DiBAl, −78 °C, toluene; (b) NaH, $(EtO)_2POCH_2CO_2C(CH_3)_3$, benzene, 25 °C (89%); (c) LDA, *p*-TsCl, THF, −78 to 25 °C (83%); (d) CpMgCl, THF, 25 °C; (e) benzene, 75 °C (81%); (f) **3**, DMAP, benzene, 25 °C; (g) 90 °C; (h) $HOCH_2CH_2OH$, *p*-TsOH·H_2O, benzene, reflux (81%); (i) O_3, $MeOH/CH_2Cl_2$, −78 °C; (j) $NaBH_4$, −78 to 25 °C (91%); (k) *n*-BuLi, $[(CH_3)_2N)_2POCl$, NEt_3, DME, 25 °C; (l) Li, *t*-BuOH, $EtNH_2$, THF, −50 to −40 °C; (m) H_2O/CH_3COCH_3, *p*-TsOH·H_2O, benzene, reflux; (n) 0.15 equiv of PDC, CH_2Cl_2, 25 °C (68%); (o) $BF_3{\cdot}Et_2O$, N_2CHCO_2Et, Et_2O, −28 °C; (p) NaCl, Me_2SO, H_2O, 150 °C (73%); (q) **3**, DMAP, Et_2O, −40 to 25 °C (93%).

Scheme II



7 **8** **9** **10**

R = t-butyl

these compounds display biological effects similar to those of their terrestrial counterparts, hirsutanes, which possess promising antibacterial and antitumor properties.[9] The key step requires the rearrangement of **7** to the corresponding cyclobutene enol ether **10**, which was then transformed into the desired product by using standard group manipulations. The regiochemistry of the (2 + 2) cycloaddition of titanaethylene to **1** (Scheme II) and the corresponding cycloreversion of **8** to **9** has been established in model studies.[10] All of the stereochemistry of the final product

(1) (a) Pine, S. H.; Zahler, R.; Evans, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3270. (b) Pine, S. H.; Pettit, R. J.; Geib, G. D.; Cruz, S. G.; Gallego, C. H.; Tijerina, T.; Pine, R. D. *J. Org. Chem.* **1985**, *50*, 1212. (c) Brown-Wensley, K. A.; Buchwald, S. L.; Cannizzo, L.; Clawson, L.; Ho, S.; Meinhart, J. D.; Stille, J. R.; Straus, D.; Grubbs, R. H. *Pure Appl. Chem.* **1983**, *55*, 1733. (d) Cannizzo, L. F.; Grubbs, R. H. *J. Org. Chem.* **1985**, *50*, 2316. (e) Clawson, L.; Buchwald, S. L.; Grubbs, R. H. *Tetrahedron Lett.* **1984**, 5733.

(2) (a) Lee, J. B.; Howard, T. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 6876. (b) Ott, K. C.; Grubbs, R. H. *Ibid.* **1981**, *103*, 5922. (c) Straus, D. A.; Grubbs, R. H. *Organometallics* **1982**, *1*, 1658.

(3) Straus, D. A.; Grubbs, R. H. *J. Mol. Catal.* **1985**, *28*, 9.

(4) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611.

(5) (a) Kinney, W. A.; Coghlan, M. J.; Paquette, L. A. *J. Am. Chem. Soc.* **1984**, *106*, 6868. (b) Wilcox, C. S.; Long, G. W.; Suh, H. *Tetrahedron. Lett.* **1984**, 395. (c) Stevenson, J. W. S.; Bryson, T. A. *Chem. Lett.* **1984**, 5.

(6) (a) Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.*, in press. (b) Swager, T. M.; Grubbs, R. H., unpublished results.

(7) Gilliom, L. R.; Grubbs, R. H. *Organometallics*, in press.

(8) For previous total syntheses of **15**, see: (a) Paquette, L. A.; Stevens, K. E. *Can. J. Chem.* **1984**, *62*, 2415 and references cited therein. (b) Crisp, G. T.; Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 7500.

(9) (a) Takeuchi, T.; Iinuma, H.; Iwanaga, J.; Takahashi, S.; Takita, T.; Umezawa, H. *J. Antibiot.* **1969**, *22*, 215. (b) Takeuchi, T.; Takahashi, S.; Iinuma, H.; Takita, T.; Maeda, K.; Umezawa, H. *Ibid.* **1971**, *24*, 631.

(10) Stille, J. R.; Grubbs, R. H., unpublished results.

0002-7863/86/1508-0855$01.50/0