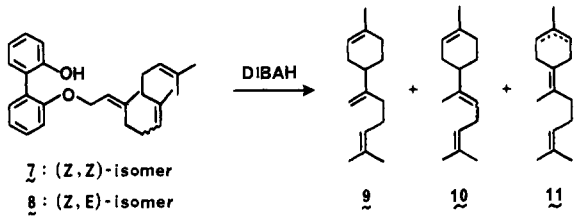
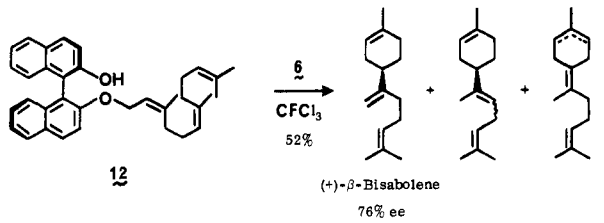
by the monosilylation and alkylation of (*R*)-(+)-binaphthol as the chiral auxiliary.[9] Reaction of **5** with DIBAH (1.2 equiv) under the standard conditions gave naturally occurring D-limonene and **3** (ratio, 5:1) in 58% yield with only moderate optical yield (~12% ee). Surprisingly, a dramatic enhancement in both regio- and enantioselectivity was observed when **5** was treated with modified organoaluminum reagents at low temperature as revealed in Table I. The highest enantioface differentiation was finally achieved by the use of (2,4,6-tri-*tert*-butylphenoxy)isobutylaluminum trifluoromethanesulfonate (**6**)[10] (3 equiv)[11] in $CFCl_3$ at −130 °C (*n*-pentane–liquid $N_2$ bath) for 3 h, producing D-limonene (54% yield) almost exclusively in 77% ee (Scheme I).

The present study has been successfully extended to the synthesis of bisabolenes[12] from biphenol (*Z,Z*)-monofarnesyl ether (**7**) and its *Z,E* isomer **8**.[13] Reaction of the *Z,Z* isomer **7** with DIBAH (1.2 equiv) at −78 °C for 30 min and at 20 °C for 4.5 h furnished β-bisabolene (**9**) preferentially in 60% yield accompanied by 16% of α-bisabolene (**10**) (*E/Z*, 2.7:1) and 9% of γ-bisabolene (**11**) (*E/Z*, 1:3).[14] On the other hand, the *Z;E* isomer **8** under the similar conditions transformed to an equal mixture of **9** (34%) and **10** (30%; *E/Z*, 2.6:1) along with **11** (7%; *E/Z*, 1:1).[15] Noteworthy is the preferential formation of **9** from




the *Z,Z* isomer **7** vs. **8**, since it implies that during deprotonation the aluminum reagent may be responsible for the discrimination of the stereochemistry of the farnesyl moiety.

Furthermore, by switching the biphenol moiety to a chiral auxiliary and manipulating the modified organoaluminum reagents, asymmetric synthesis of bisabolenes appears feasible. Thus, exposure of (*R*)-(+)-binaphthol (*Z,Z*)-monofarnesyl ether (**12**)[16] ($[\alpha]^{20}_D$ +28.6° (*c* 1.02, THF)) to the aluminum reagent **6** (3 equiv) in $CFCl_3$ at −130 °C for 3 h led to the formation of bisabolenes (ratio of *Z*-α/β/*Z*-γ/*E*-γ/*E*-α = 1:90:4:1:25) in 52% yield, from which (+)-β-bisabolene was separated by preparative TLC on $AgNO_3$-impregnated silica gel (ether/hexane, 1:10 as eluant).[17] This product was 76% enantiomerically pure, as determined by the comparison of the magnitude of the optical rotation, $[\alpha]^{20}_D$ +56° (*c* 2.94, EtOH), with that of authentic sample.[18,19]




The terpene syntheses disclosed above provide a new body of results that, coupled with certain other considerations, (1) indicate that the six-membered ring is formed with a high degree of neighboring π-bond participation during C–O heterolysis of **5** and **12**, thus allowing the remote chiral transfer efficiently and (2) suggest that the overall process may involve conformationally rigid cationic structures. The origin of the high enantioselection arising from the rigid, unique conformation of the chiral acyclic precursor must await further research.

**Acknowledgment.** Support for this research from the Ministry of Education, Japanese Government (Grand-in-aid 57102008), and Kuraray Co., Ltd., is gratefully acknowledged. We thank Professor R. Noyori for valuable discussions.

**Registry No.** (*Z*)-**1**, 86803-76-1; (±)-**2**, 7705-14-8; **3**, 586-62-9; (*Z*)-**4**, 86803-77-2; (*R*)-(*Z*)-**5**, 86851-45-8; **6**, 86822-06-2; (*Z,Z*)-**7**, 86803-78-3; (*Z,E*)-**8**, 86803-79-4; (±)-**9**, 4891-79-6; (±)-(*E*)-**10**, 70286-16-7; (±)-(*Z*)-**10**, 70332-15-9; (*E*)-**11**, 53585-13-0; (*Z*)-**11**, 13062-00-5; (*R*)(*Z,Z*)-**12**, 86803-80-7; *i*-$Bu_2AlOTf$, 86803-81-8; *i*-$BuAl(OTf)_2$, 86803-82-9; D-limonene, 5989-27-5; (+)-β-bisabolene, 20377-48-4; 2,6-bis(*tert*-butyl)-4-methylphenoxyisobutylaluminum trifluoromethanesulfonate, 86803-83-0; (*R*)-(*Z*)-α-bisabolene, 70286-33-8; (*R*)-(*E*)-α-bisabolene, 70286-31-6; (*R*)-(+)-binaphthol, 18531-94-7; (*R*)-(+)-binaphthol monosilyl ether, 86803-84-1; dimethylaluminum 2,6-di-*tert*-butyl-4-methylphenoxide, 86803-85-2; (*Z*)-neryl bromide, 25996-10-5.

(9) Cram, D. J.; Cram, J. M. *Acc. Chem. Res.* **1978**, *11*, 8. Recently a highly enantioselective reducing agent using chiral binaphthol was reported: Noyori, R. *Pure Appl. Chem.* **1981**, *53*, 2315.

(10) For preparation of the reagent **6**, see: Yamamura, Y.; Umeyama, K.; Maruoka, K.; Yamamoto, H. *Tetrahedron Lett.* **1982**, *23*, 1933.

(11) The use of 1.2 equiv of **6** gave the unreproducible results.

(12) Recent bisabolene syntheses: (a) Crawford, R. J.; Erman, W. F.; Broaddus, C. D. *J. Am. Chem. Soc.* **1972**, *94*, 4298. (b) Faulkner, D. J.; Wolinsky, L. E. *J. Org. Chem.* **1975**, *40*, 389. (c) Wolinsky, L. E.; Faulkner, D. J.; Finer, J.; Clardy, J. *Ibid.* 1976, *41*, 697. (d) Larkin, J. P.; Nonhebel, D. C.; Wood, H. C. S. *J. Chem. Soc., Perkin Trans. 1* **1976**, 2524. (e) Kobayashi, S.; Tsutsui, M.; Mukaiyama, T. *Chem. Lett.* **1977**, 1169. (f) Delay, F.; Ohloff, G. *Helv. Chim. Acta* **1979**, *62*, 369. (g) Becker, M.; Weyerstahl, P. *Ibid.* **1979**, *62*, 2724.

(13) The ethers **7** and **8** were obtained in 50–55% yield by the procedure similar to that described in ref 6. (*Z,Z*)-Farnesol and its *Z,E* isomer were kindly provided from Kuraray Co., Ltd.

(14) The structures **9**–**11** were confirmed by the capillary GLC comparison (20-m OV-101, 150 °C) with the authentic samples: $t_r$((*Z*)-**10**) = 18.37 min; $t_r$(**9**) = 19.05 min; $t_r$((*Z*)-**11**) = 19.53 min; $t_r$((*E*)-**11**) = 20.72 min; $t_r$((*E*)-**10**) = 21.49 min. The authentic **9** and **11** were prepared according to ref 12, a and c, respectively. The synthesis of authentic **10** was made by the analogous method as in ref 12c.

(15) Cyclization of **7** and **8** by using dimethylaluminum 2,6-di-*tert*-butyl-4-methylphenoxide showed a similar tendency. The yields and ratios of bisabolenes thus obtained are as follows: **7**: 64% ((*Z*)-**10**/**9**/(*Z*)-**11**/(*E*)-**11**/(*E*)-**10** = 1:18:2.3:1:3.3); **8**: 79% (1.3:6.5:1:1.1:4.3).

(16) The ether **12** was synthesized in 50–52% yield in a like manner as described in ref 8.

(17) Attempted isolation of chiral (+)-(*E*)-α-bisabolene was unsuccessful.

(18) See ref 12a.

(19) The *Z,E* isomer of **12** was subjected to the analogous cyclization conditions providing (+)-β-bisabolene in lower optical yield (62% ee).

## In Situ Trapping of Ortho-Lithiated Benzenes Containing Electrophilic Directing Groups[1]

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*Received April 26, 1983*

The directed ortho lithiation of substituted benzenes is a powerful method for the preparation of synthetically useful aryllithium intermediates.[2] It is used with benzene rings containing kinetically acidic C–H bonds ortho to nonelectrophilic directing groups, such as the methoxyl substituent. It can be used with electrophilic directing groups if the electrophilic center reacts sufficiently slowly with the nucleophilic base (usually *n*-butyllithium) or with the product aryllithium. Two methods have been used to slow this reaction sufficiently to allow the accumulation of synthetically useful concentrations of the aryllithium before addition of the external electrophile to give the desired product: (a) the use of low temperatures (usually −78 °C or lower) and/or (b) the use of electronically deactivated electrophiles, such as amides,[2b] or sterically deactivated electrophiles, such as the 4,4-dimethyl-2-oxazolines.[3] We here report a third stratagem to minimize

(1) Krizan, T. D.; Martin, J. C. "Abstracts of Papers", 185th National Meeting of the American Chemical Society, Seattle, WA, March 20–25, 1983; American Chemical Society: Washington, D.C., 1983; ORGN 116.

(2) For recent reviews, see: (a) Gschwend, H. W.; Rodriguez, H. R. *Org. React.* **1979**, *26*, 1. (b) Beak, P.; Snieckus, V. *Acc. Chem. Res.* **1982**, *15*, 306.

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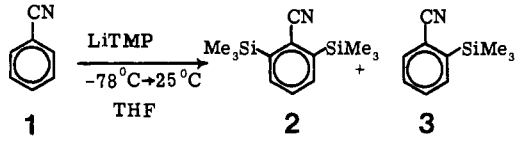
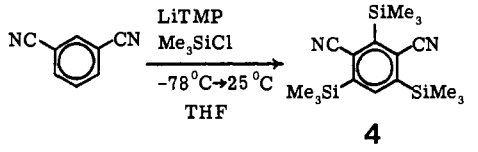
unwanted reactions between the aryllithium and electrophilic directing groups—in situ trapping of the aryllithium by electrophilic traps present during deprotonation of the substituted benzene by a very sterically encumbered base (e.g., lithium 2,2,6,6-tetramethylpiperidide, LiTMP).[4] This method is effective when deprotonation of the substituted benzene is faster than reaction of the hindered base with the in situ electrophilic trap, and the reaction of the resulting aryllithium intermediate with the trap is faster than its reaction with the substituted benzene.

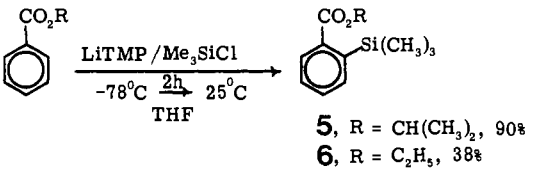
Although 1,3-dicyanobenzene is rapidly lithiated at the 2-position by lithium diisopropylamide (LDA) at temperatures below −90 °C,[5] a temperature at which the intermediate aryllithium is stable enough to allow its subsequent reaction with electrophiles to occur in high yield, benzonitrile (**1**) is not deprotonated under these conditions. Use of the more basic LiTMP[6] at −78 °C results in the formation of 2-lithiobenzonitrile.[7] Subsequent additions of electrophiles result in rather low overall yields of 2-substituted benzonitriles.[8] The in situ trapping method described in this paper results in greatly increased yields of substituted benzonitriles.[9]

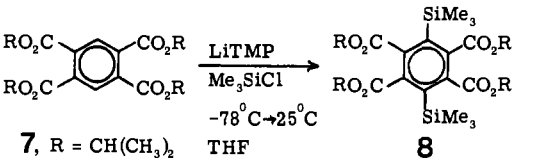
In a typical procedure, substrate (S) **1** (1.94 mmol) was added at −78 °C to a tetrahydrofuran (THF, 20 mL) solution containing both the base (B) used in this research, LiTMP (5.82 mmol) and the electrophilic trap (T) trimethylsilyl chloride (TMSCl, 11.64 mmol) (S:B:T = 1:3:6). The solution was slowly warmed to 25 °C after 15 min to yield 86% of **2**.[10] Mixing the reagents (S:B:T = 1:2.2:10) at 0 °C provides 65% of **2** and 35% of **3**. Under the same conditions, a reaction in which the trap was omitted gave a very complex mixture of products, suggesting that 2-lithiobenzonitrile is very short-lived under these conditions. Under similar conditions, 1,3-dicyanobenzene undergoes three ortho trimethylsilylations to give 93% of **4** (mp 194–197 °C).




The greater ease of hydrolysis of the ester function, relative to the nitrile function, makes alkylbenzoates more attractive precursors for 2-substituted benzoic acids. Upton and Beak[11] have shown that ortho lithiation of alkylbenzoates by LiTMP occurs at −78 °C, but the intermediate aryllithium is rapidly destroyed to give 2-benzoylbenzoates and other self-condensation products before the desired electrophilic reaction partner can be introduced. Under our conditions for in situ trapping with TMSCl at −78 °C (S:B:T = 1:1.2:10), substrate isopropyl benzoate gives 90% of **5**. The less sterically hindered ethyl ester gives only 38% of **6** under these conditions, presumably because the faster self-condensation reactions compete with the trapping with TMSCl. Disilylation of **7** to give 48% of **8** (mp 283–284 °C) occurred with S:B:T =

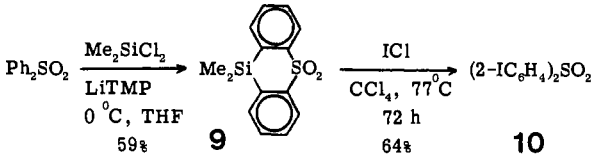



1:2.2:10 at −78 °C. The ketonic substrate pivalophenone, with S:B:T = 1:2.2:10 at −78 °C, gave 59% of 2-(trimethylsilyl)pivalophenone, with no disilylation product.

Other electrophiles are also effective as in situ traps. For example, trimethyl borate acts as a trap with substrate **1** (S:B:T = 1:2.2:2.2) to give an intermediate arylboronate which reacts with $H_2O_2$ in acetic acid–THF to give 22% of 2-cyanophenol. (No 2,6-dihydroxybenzonitrile was detected.) Hexafluoroacetone (HFA) is also very effective as an in situ trap with LiTMP, giving nearly quantitative yields of products from addition of the intermediate aryllithium to the reactive carbonyl of HFA in reactions with substrate pyridines and pyridine 1-oxides.[12]

The use of dimethyldichlorosilane as an in situ trap in the lithiation of diphenyl sulfone (S:B:T = 1:2:1) at 0 °C, gives cyclic silane **9** in 59% conversion (by NMR).[13] The reaction of **9** with ICl to give **10**[14] in 64% yield gives overall 38% conversion of the diphenyl sulfone to its 2,2′-diiodo derivative, **10**.




The susceptibility of the C–Si bond to electrophilic cleavage,[15] as illustrated by the conversion of **9** to **10**, expands the synthetic potential for in situ trapping with chlorosilanes. For example, reaction of **2** with ICl as above gave 88% of the hitherto unreported 2,6-diiodobenzonitrile (mp 167–169 °C).[16]

We have described successful in situ trapping, using the electrophilic traps TMSCl, dimethyldichlorosilane, and trimethyl borate, of aryllithium species derived from the reaction of the hindered base LiTMP, in the presence of the trap, with representative substrates including benzonitriles, benzoate esters, aryl ketones, and aryl sulfones. Extension of the in situ trapping technique to other types of substrates,[12] traps,[12] and hindered bases[19] has an enormous potential for the efficient synthesis of

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(9) See: Marsais, F.; Laperdrix, B.; Güngör, T.; Mallet, M.; Quéguiner, G. *J. Chem. Res., Miniprint* **1982**, 2863, for other evidence that lithiation of aryl rings can be carried out in the presence of $(CH_3)_3SiCl$.
(10) Satisfactory analytical data (±0.4% for C, H, and when appropriate, N), mass spectra (70 eV), and $^1H$ NMR spectra were obtained for all new compounds reported in this paper, and yields are for isolated materials unless otherwise stated. All experiments were run at approximately the same concentration of substrate as in this example.
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(15) Eaborn, C. *J. Organomet. Chem.* **1975**, *100*, 43.
(16) With electron-withdrawing groups ortho to the trimethylsilyl group, as in the products reported in this paper, it has been reported that the trimethylsilyl group can be cleaved by the nucleophilic attack of cesium fluoride[17] or potassium *tert*-butoxide[18] at silicon, providing another possible route for the replacement of the trimethylsilyl group with other functional groups.
(17) Mills, R. J.; Snieckus, V. *J. Org. Chem.* **1983**, *48*, 1565.
(18) Effenberger, F.; Spiegler, W. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 265.

1,2-disubstituted and 1,2,3-trisubstituted aromatic hydrocarbons.

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(19) Traditional lithiation procedures must employ lithiating agents basic enough to convert the carbon acid largely to its conjugate base. The in situ trapping procedure can be useful with weaker bases if the deprotonation, to produce a small concentration of trappable aryllithium, is sufficiently rapid to make this process competitive in rate with reaction of the hindered base with the in situ electrophile.

## Synthesis and Chemistry of Chiral Vinyl Rhenium Complexes ($\eta$-$C_5H_5$)Re(NO)($PPh_3$)(CH=CHR). Stereoselective Reactions with Electrophiles and a Spontaneous Alkylidene to Olefin Rearrangement

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There has been a recent surge of interest in asymmetric organic synthesis via deprotonated chiral enamines ($RCH{=}C(R')NR_{asym}^-$) and related nucleophiles.[2] Surprisingly, little attention has been given to potential synthetic applications of vinyl complexes of electron-rich metals, $L_nMCH{=}CHR$ (**1**).[3,4] Electrophilic ($E^+X^-$) attack upon **1** would be expected to initially yield the alkylidene $L_nM^+{=}CHCHREX^-$. In the case of a chiral $L_nM$ moiety, the new chiral center (CHRE) might be formed with appreciable asymmetric induction. In view of the remarkably stereospecific transformations[5,6] that have been observed with easily resolved[7]

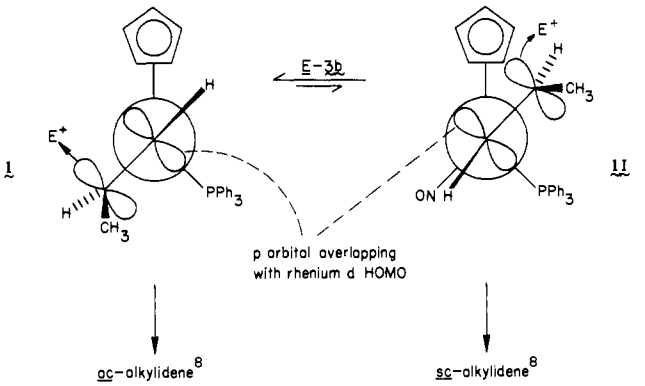
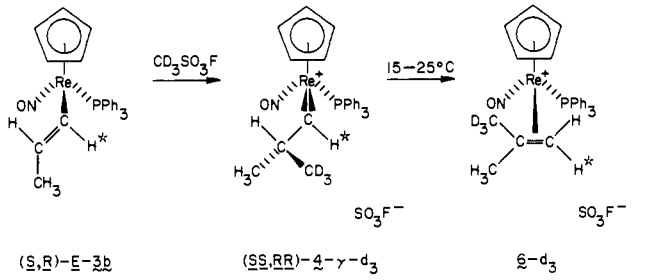


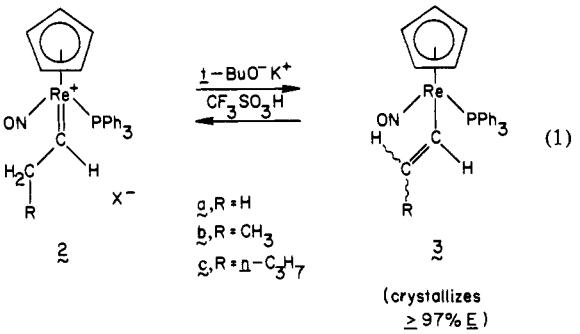

**Figure 1.** Proposed principal modes of electrophilic attack upon *E*-**3b**.

Scheme I. Stereoselective Synthesis and Rearrangement of an Isobutylidene Complex




chiral ($\eta$-$C_5H_5$)Re(NO)($PPh_3$)(X) compounds, we set out to probe the reactivity of ($\eta$-$C_5H_5$)Re(NO)($PPh_3$)(CH=CHR) complexes and describe below the title observations.

Reaction of alkylidenes **2a–c** ($PF_6^-$ salts; ca. 90:10 equilibrium mixtures of *ac*/*sc* Re=C isomers[5c,8]) with 1.1–1.4 equiv of *t*-$BuO^-K^+$ gave, after workup, vinyl complexes **3a–c** in 70–80% yields (eq i).[9] Propenyl and pentenyl complexes **3b** and **3c**




(1)

crystallized as >97:3 mixtures of *E*/*Z* geometric isomers but easily equilibrated (3 h, 25 °C, $CDCl_3$; 3 min, −75 °C, 0.25 equiv $CHCl_2CO_2H$) to (84 ± 2):(16 ± 2) and (92 ± 2):(8 ± 2) *E*/*Z* mixtures, respectively.

When **3a–c** were treated with 1.1 equiv of $CF_3SO_3H$ in $CD_2Cl_2$ at −78 °C, alkylidenes **2a–c** formed in quantitative $^1H$ NMR yields as (71 ± 2):(29 ± 2), (90 ± 2):(10 ± 2), and (88 ± 2):(12 ± 2) mixtures of *ac*/*sc* Re=C isomers,[8] respectively. Interestingly, addition of 1.03 equiv of $CHCl_2CO_2H$ ($pK_{a(H_2O)}$ = 1.26) to **3b** in $CD_2Cl_2$ at −68 °C gave a (66 ± 2):(34 ± 2) equilibrium **2b**/**3b** ratio. Thus the $\beta$-hydrogens of **2b** are acidic enough to be appreciably abstracted by the weak base $CHCl_2CO_2^-$.[10]

(1) (1) Address correspondence to this author at the University of Utah; Fellow of the Alfred P. Sloan Foundation (1980–1984) and Camille and Henry Dreyfus Teacher-Scholar Grant Recipient (1980–1985).

(2) (a) Mēa-Jacheet, D.; Horeau, A. *Bull. Soc. Chim. Fr.* **1968**, 4571. (b) Meyers, A. I. *Pure Appl. Chem.* **1979**, *51*, 1255. (c) Meyers, A. I.; Williams, D. R.; Erickson, G. W.; White, S.; Druelinger, M. *J. Am. Chem. Soc.* **1981**, *103*, 3081. (d) Whitesell, J. K.; Whitesell, M. A. *J. Org. Chem.* **1977**, *42*, 377. (e) Davenport, K. G.; Eichenauer, H.; Enders, D.; Newcomb, M.; Bergbreiter, D. E. *J. Am. Chem. Soc.* **1979**, *101*, 5654. (f) Enders, D.; *CHEMTECH* **1981**, *11*, 504 and references IBC, November issue. (g) Evans, D. A.; Ennis, M. D.; Mathre, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 1737. (h) Saigo, K.; Kasahara, A.; Ogawa, S.; Nohira, H. *Tetrahedron Lett.* **1983**, *24*, 511.

(3) See, inter alia, the following papers and references cited therein: (a) Reger, D. L.; McElligott, P. J. *J. Am. Chem. Soc.* **1980**, *102*, 5923. (b) Bodnar, T.; Cutler, A. R. *J. Organomet. Chem.* **1981**, *213*, C31. (c) Casey, C. P.; Miles, W. H.; Tukada, H.; O'Connor, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 3761. (d) Kremer, K. A. M.; Kuo, G.-H.; O'Connor, E. J.; Helquist, P.; Kerber, R. C. *Ibid.* **1982**, *104*, 6119. (e) Reger, D. L.; Belmore, K. A.; Mintz, E.; Charles, N. G.; Griffith, E. A. H.; Amma, E. L. *Organometallics* **1983**, *2*, 101. (f) Grötsch, G.; Malisch, W. *J. Organomet. Chem.* **1983**, *246*, C49.

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(5) (a) Kiel, W. A.; Lin, G.-Y.; Gladysz, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 3299. (b) Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *Ibid.* **1982**, *104*, 4865. (c) Kiel, W. A.; Lin, G.-Y.; Bodner, G. S.; Gladysz, J. A. *Ibid.* **1983**, *105*, 4958. (d) Merrifield, J. H.; Lin, G.-Y.; Kiel, W. A.; Gladysz, J. A. *Ibid.* **1983**, *105*, 5811.

(6) Wong, A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4948.

(7) Merrifield, J. H.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1204.

(8) (a) *Pure Appl. Chem.* **1976**, *45*, 11. See section E-5.6, p 24. Synclinal (*sc*) Re=C isomers are those in which the highest priority[8b] ligands on Re ($C_5H_5$) and C (R) define a 60 ± 30° torsion angle. Anticlinal (*ac*) isomers are those in which the highest priority ligands define a 120 ± 30° torsion angle. (b) Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 6598. Sloan, T. *Top. Stereochem.* **1981**, *12*, 1.

(9) Spectroscopic features of **3–7** are routine,[5-7] and full characterization is provided in the supplementary material.

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