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

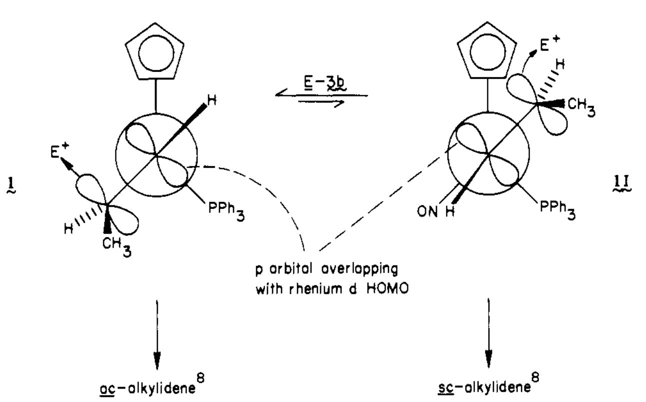
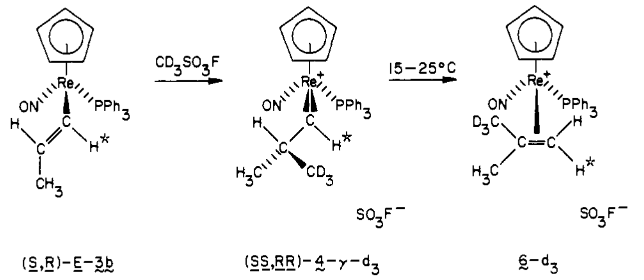
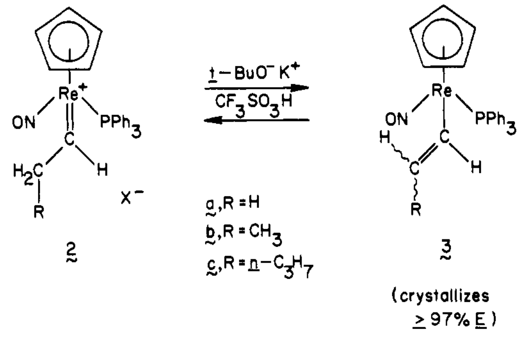


Figure 1. Proposed principal modes of electrophilic attack upon *E*-**3b**.

Scheme I. Stereoselective Synthesis and Rearrangement of an Isobutylidene Complex



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** 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.



(1)

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 β-hydrogens of **2b** are acidic enough to be appreciably abstracted by the weak base $CHCl_2CO_2^-$.[10]

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(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).

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

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The nucleophilicity of **3**, coupled with the low C=C rotational barriers,[11] suggests that zwitterionic resonance forms Re^+=CH—C^-HR contribute significantly to the ground state of **3**. In view of the established geometry of the d donor orbital on rhenium,[5b] we propose that electrophilic attack occurs via the conformers I and II shown in Figure 1. These conformers would yield *ac* and *sc* Re=C isomers, respectively.

The feasibility of effecting 1,3-asymmetric induction was first assayed by treating *E*-**3b** with 1.03 equiv of CF_3SO_3D in CD_2Cl_2 at −75 °C. The relative NMR integrations of the β-hydrogens in the resulting *ac*-**2b**-β-d_1 indicated a (76 ± 5):(24 ± 5) ratio of diastereomers. Thus protonation occurs preferentially upon one C=C face of I. By analogy to the behavior of other (η-C_5H_5)Re(NO)(PPh_3)(X) compounds,[5b,6] we suggest that the face anti to the PPh_3 ligand is more reactive (Figure 1). However, analysis of the *E*-**3b**/CF_3SO_3D reaction is complicated by the formation of some *sc*-**2b**-β-d_1 (vide supra) and **2b**-β-d_2 (ca. 20%), so we sought a carbon–carbon bond-forming reaction in which to measure stereoselectivity.

Reaction of *E*-**3b** (0.1 M in CH_2Cl_2, −25 °C, 15 min) with 10 equiv of CH_3SO_3F gave, after workup at −25 °C, isobutylidene *ac*-[(η-C_5H_5)Re(NO)(PPh_3)(=CHCH(CH_3)$_2$)]$^+$ SO_3F^- (*ac*-**4**, only one Re=C isomer observed) as a thermally unstable oil of >95% ^{1}H NMR purity in 65% spectroscopic yield. Two CH_3 ^{1}H NMR resonances[9] were present. The corresponding reaction of *E*-**3b** with CD_3SO_3F was ^{1}H NMR monitored. Initial equilibration of *E*-**3b** to the 84:16 *E*/*Z* mixture occurred, followed by methylation to *ac*-**4**-γ-d_3 (Scheme I). Integration of the CH_3 ^{1}H NMR resonances indicated a (92 ± 2):(8 ± 2) ratio of diastereomers. The major diastereomer was assigned the (*SS*,*RR*) configurations by assuming (as reasoned above) the mode of attack upon I shown in Figure 1.

The isolation of **4** was complicated by two factors. First, as in enolate and enamine chemistry,[12] polyalkylation/proton transfer side reactions occurred when careful conditions were not followed. This problem could be circumvented by deprotonating (10 equiv *t*-BuO^-K^+) crude **4** to (η-C_5H_5)Re(NO)(PPh_3)(CH=C(CH_3)$_2$) (**5**, 60% isolated).[9] Treatment of **5** with HBF_4·ether at −78 °C gave pure solutions of **4**. Second, **4** underwent a stereoselective isobutylidene → isobutylene (**6**, 73% isolated) rearrangement near room temperature (Scheme I).

The rearrangement **4** → **6** followed the rate law $d[\mathbf{4}]/dt = -k_{obsd}[\mathbf{4}]$. Data obtained in CD_2Cl_2 at 276, 288, 293, and 298 K gave $\Delta H^* = 20.4 \pm 1.4$ kcal/mol and $\Delta S^* = -2.7 \pm 0.3$ eu. Rearrangement of the 92:8 mixture of **4**-γ-d_3 diastereomers gave **6**-d_3 with 89 ± 3% of the CD_3 label in the upfield (^{1}H NMR)[5c,9] methyl site. Rearrangement of **4**-α-d_1 (prepared via **2b**-α-d_1;[5c] H* in Scheme I) gave **6**-d_1 with 91 ± 5% of the D label in the downfield =CHH′ site. Homonuclear NOE experiments on **6** showed the downfield CH_3 to be cis to the downfield =CHH′ hydrogen. Hence the hydrogen migrates to a position cis to the pro-*S* methyl group of **4**. The conversion **4** → **6** is reminiscent of a Wagner–Meerwein-like 1,2-hydrogen shift, but the high stereoselectivity suggests that $\pi_2s + \sigma_2a$ (Re=C/CH) or $\pi_2a + \sigma_2s$ mechanisms should be considered. Recently, several unstable alkylidene complexes have been observed to decompose similarly.[3c,d,13]

Vinyl complexes **3a–c** underwent reactions with other classes of electrophiles. Treatment of **3b** and **3c** with peracid *m*-$ClC_6H_4CO_3H$ in $CHCl_3/K_2CO_3$ gave carbon-bound rhenium enolates (or β-oxoalkyls) (η-C_5H_5)Re(NO)(PPh_3)(CH_2COR) (R = CH_3, **7b**; R = *n*-C_3H_7, **7c**)[9] in 40–50% yields. One possible pathway for this transformation would entail heterolytic opening of an epoxide intermediate to a Re^+=CHCHRO^- species, followed by a 1,2-hydride migration similar to **4** → **6**. Complexes **3a–c** are also attacked by electrophilic olefins and metal alkylidenes; details of these reactions will be reported separately.

In summary, we have shown that chiral vinyl rhenium complexes can undergo electrophilic attack with appreciable 1,3-asymmetric induction. Although **3a–c** react only with strong electrophiles, it can be predicted that L_nM_{asym}–C(X)=CHR species of greater nucleophilicity (e.g., X = oxygen substitutent)[14] should be of considerable value in synthesis. Finally, a two-step alkene → alkylidene rearrangement has recently been proposed as an initiating step in olefin metathesis.[15] In view of the microscopic reverse of **4** → **6**, such transformations could well be concerted and stereoselective.

Acknowledgment. We thank the Department of Energy and the NIH (GM 29026-01) for supporting the synthetic and stereochemical aspects of this study, respectively. FT NMR spectra were recorded on spectrometers obtained via NSF departmental instrumentation grants.

Supplementary Material Available: Tables of spectroscopic and other characterization of **3–7** (4 pages). Ordering information is given on any current masthead page.

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[11] Facile C=C rotation has also been noted in RCH=$CHNR^-$ compounds (ΔG^* = 17–22 kcal/mol. Lee, J. Y.; Lynch, T. J.; Mao, D. T.; Bergbreiter, D. E.; Newcomb, M. *J. Am. Chem. Soc.* **1981**, *103*, 6215) and (η-C_5H_5)Fe(CO)(PPh_3)(CR=CHR) complexes.[3a]

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Observation of 2-Azabicyclo[3.2.1]oct-1-ene, a Highly Reactive Bridgehead Imine

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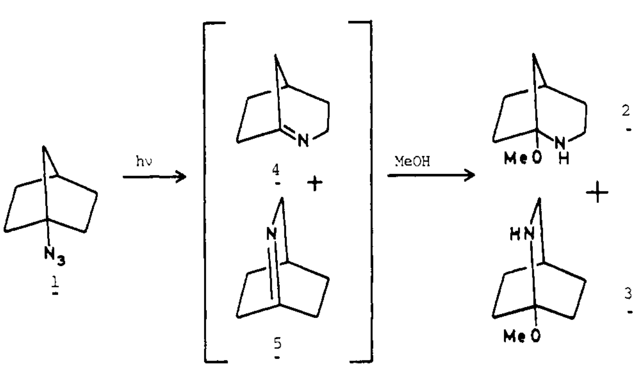
Interest in compounds containing bridgehead imine functionality has recently surged. In 1971 Reed and Lwowski[2] reported that irradiation of 1-azidobicyclo[2.2.1]heptane (**1**) in methanol gave adducts **2** and **3** in the ratio of 2:1, consistent with trapping of imines **4** and **5**. Whether or not a discrete nitrene is involved in these rearrangements is an open question, although some evidence points toward alkyl migration in concert with nitrogen loss.[3] In subsequent years similar evidence has accumulated for a number of anti-Bredt imines, generated by thermal and photo-



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