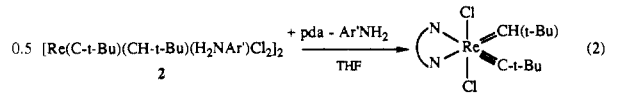
ligand lies in the C/Re/C plane and the *tert*-butyl group of the neopentylidene ligand points toward the neopentylidyne ligand (syn orientation). Reaction of **2** with 2 equiv of phenylenediamine (pda) in tetrahydrofuran or methylene chloride at room temperature yields $Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(pda)Cl_2$ (**3**, eq 2) in 95% yield.[6] One possible configuration (based on NMR data) is that



shown in eq 2. **3** reacts with excess HCl gas in dimethoxyethane at room temperature to yield $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)Cl_2]_x$ (**4**, eq 3) in 85% yield.[7] **4** is believed to be a polymer in the solid state, but it is soluble in dimethoxyethane and therefore easily separated from virtually insoluble pda·2HCl.

$$3 + \text{excess HCl} \xrightarrow[\text{DME}]{} \underset{\mathbf{4}}{[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)Cl_2]_x} + \text{pda·2HCl} \quad (3)$$

Addition of 2 equiv of potassium hexafluoro-*tert*-butoxide to **4** suspended in dichloromethane at 25 °C affords $Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)[OCMe(CF_3)_2)]_2$ (**5**) quantitatively as an orange oil.[8] Although **5** decomposes slowly when isolated, it appears to be stable indefinitely in solution at concentrations of ~10 mM. It is presumably a pseudotetrahedral species in which the *tert*-butyl group of the neopentylidene ligand points toward the neopentylidyne ligand (syn orientation).[2b,3a]

Ten equivalents of *cis*-3-hexene reacts with **5** in C_6D_6 in 7 h at 25 °C to give a product quantitatively versus an internal standard whose ^1H and ^{13}C NMR spectra[9] are consistent with it being two isomers of $Re(C\text{-}t\text{-}Bu)(CHEt)[OCMe(CF_3)_2]_2$. It is important to note that the neopentylidyne ligand is unaltered, a fact that suggests that proton transfer from an alkylidene ligand to the neopentylidyne ligand is slow and that the neopentylidyne ligand therefore is an ancillary ligand in this reaction. We propose that the isomers of $Re(C\text{-}t\text{-}Bu)(CHEt)[OCMe(CF_3)_2]_2$ are syn and anti alkylidene rotamers, the anti rotamer being that in which the ethyl group of the propylidene ligand points away from the neopentylidyne ligand. Complexes of the type $M(CHR')(NAr)(OR)_2$ (M = Mo[2b] or W[10]) are also believed to form rotamers.

Compound **5** is an effective catalyst for the metathesis of internal and functionalized olefins. The activity of **5** is limited by its relatively slow reaction with olefin, but the rate of metathesis increases appreciably when a smaller alkylidene ligand is formed. For example, **5** metathesized 100 equiv of *cis*-2-pentene in benzene to an equilibrium mixture (1:2:1) of 2-butenes, 2-pentenes, and 3-hexenes in 2.5 h at 25 °C. Another 100 equiv of *cis*-2-pentene was then added and was equilibrated in less than 30 min.

Methyl oleate reacts slowly with **5**. Methyl oleate (5 equiv) in C_6D_6 converted 40% of **5** to two new alkylidene complexes in 12 h, according to proton NMR spectra. A reaction involving 50 equiv of methyl oleate with **5** in dichloromethane required 12 h to reach equilibrium [1:2:1 mixture of $Me(CH_2)_7CH{=}CH(CH_2)_7Me$, $Me(CH_2)_7CH{=}CH(CH_2)_7CO_2Me$, and $MeO_2C(CH_2)_7CH{=}CH(CH_2)_7CO_2Me$]. After 24 h, another 50 equiv of methyl oleate was added to this solution, and equilibrium was reached in 7.5 h. When **5** was first treated with 10 equiv of *cis*-3-hexene for several hours and then 50 equiv of methyl oleate was added, equilibrium was reached in 3 h. An additional 100 equiv of methyl oleate added to this mixture was equilibrated in 6 h.

To our knowledge, this is the first time that olefin metathesis by rhenium alkylidene complexes has been proven.[11] Until now, only heterogeneous Re metathesis catalysts had been prepared, and the oxidation state of the metal was not known.[1] We currently are studying modification of the ligands in this system, polymerization of cyclic olefins and acetylenes, metathesis of functionalized olefins, and pathways of catalyst deactivation.

Acknowledgment. R.R.S. thanks the National Science Foundation for support through Grant CHE 88-22508.

(6) 1,2-Phenylenediamine (0.31 g, 2.9 mmol) was added to $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(H_2NAr')Cl_2]_2$ (1.5 g, 1.45 mmol) in 40 mL of THF. The orange solution rapidly darkened, and after 25 min, the solvent was removed in vacuo. The resulting pale orange solid was washed with pentane and then twice reprecipitated from 10 mL of THF with pentane, to give 1.39 g of product (95%): ^1H NMR (CD_2Cl_2) δ 13.52 (s, 1, C*H*-*t*-Bu), 7.31 (m, 4, H_{aryl}), 4.74 (br s, 4, NH_2), 1.38 and 1.32 (s, 9, C-*t*-*Bu*); ^{13}C NMR (CD_2Cl_2) δ 295.6 (*C*-*t*-Bu), 292.0 (*C*H-*t*-Bu, J_{CH} = 118 Hz), 138.1 ($C_{1,2}$), 130.1, 129.0, 128.4, and 127.5 (C_{3-6}), 52.9 and 47.0 (CMe_3), 31.2 and 28.1 (CMe_3).

(7) Addition of HCl(g) (98 mL, 4.4 mmol) via syringe to a dimethoxyethane solution of **3** (1.0 g, 1.98 mmol) yielded a white precipitate immediately. After 20 min, the precipitate was removed by filtration and the orange filtrate reduced to dryness in vacuo. The resulting solid was washed with pentane, to afford a pale orange powder (0.67 g, 85%), which is insoluble in all but strongly coordinating solvents: ^1H NMR (THF-d_8) δ 13.26 (s, 1, C*H*-*t*-Bu), 1.35 and 1.26 (s, 9, C-*t*-Bu); ^{13}C NMR (THF-d_8) δ 293.9 (*C*-*t*-Bu), 285.8 (*C*H-*t*-Bu, J_{CH} = 125 Hz), 53.59 and 46.66 (CMe_3), 31.4 and 28.4 (CMe_3). Anal. Calcd for $C_{10}H_{19}Cl_2Re$: C, 30.30; H, 4.83. Found: C, 30.21; H, 4.84.

(8) ^1H NMR (C_6D_6): δ 11.05 (s, 1, C*H*-*t*-Bu), 1.15 and 1.13 (s, 9, C-*t*-*Bu*), 1.11 [s, 6, $OC(CF_3)_2Me$]. ^{13}C: δ 295.8 (*C*-*t*-Bu), 248.8 (*C*H-*t*-Bu, J_{CH} = 127 Hz), 54.8 and 45.3 (*C*-*t*-Bu), 31.9 and 29.9 (CMe_3). Related bisalkoxide derivatives in which OR = O-*t*-Bu,[4a] O-2,6-C_6H_3-*i*-Pr_2, O-2,6-$C_6H_3Me_2$, and $OCMe_2(CF_3)$ have also been prepared. They will be discussed in later publications.

(9) ^1H NMR (C_6D_6, major, minor): δ 11.36, 12.42 (t, 1, C*H*Et, J_{HH} = 6, 9 Hz), 4.03, 3.71 (dq, 2, $CHCH_2Me$). ^{13}C (CD_2Cl_2): δ 299.7, 303.2 (*C*-*t*-Bu), 245.2, 245.0 (*C*HEt, J_{CH} ~ 126 Hz), 55.9, 33.1 ($CCMe_3$), 35.4, 48.2 ($CHCH_2Me$).

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(11) (a) Some metathesis activity, presumably homogeneous, starting with a characterized alkylidene complex has been observed before,[11b] although the nature of the active species could not be determined. (b) Edwards, D. S. Ph.D. Thesis, MIT, 1983.

Stepwise Mechanism of Formal 1,5-Sigmatropic Rearrangement of Dimethyl 3,3-Dialkyl-3*H*-pyrazole-4,5-dicarboxylates

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Intramolecular migrations of atoms or groups from an sp^3 carbon to a proximate sp^2 atom of a five-membered, four-π-electron ring are well recognized. Probably the most familiar of such rearrangements is the migration of a hydrogen atom around the cyclopentadiene ring[1] that rapidly interconverts 5-alkylcyclopentadienes with their 1-alkyl and 2-alkyl isomers, Scheme I. Similar H migrations are common in acyclic conjugated diene systems,[2-4] and there are examples also of analogous migrations of alkyl,[2,3,5] aryl,[2,3,6] acyl,[2,7] vinyl,[3] alkynyl,[8] and cyano[8] groups.

* Author to whom correspondence may be addressed.

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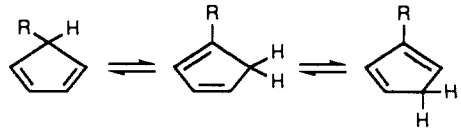
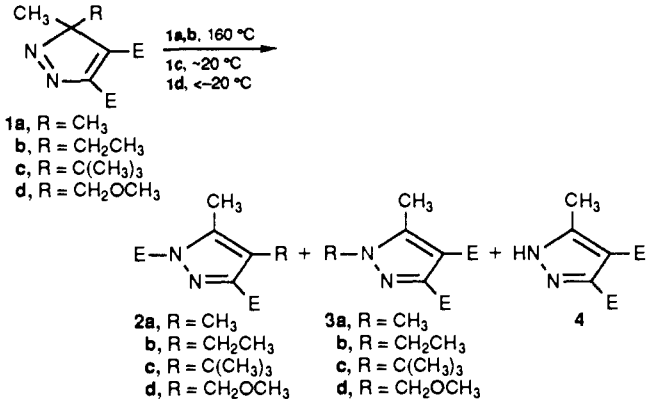
Scheme I

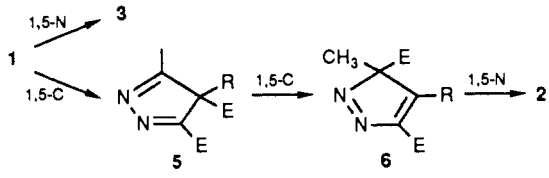


Scheme II[a]



[a] E = CO_2CH_3.

Scheme III

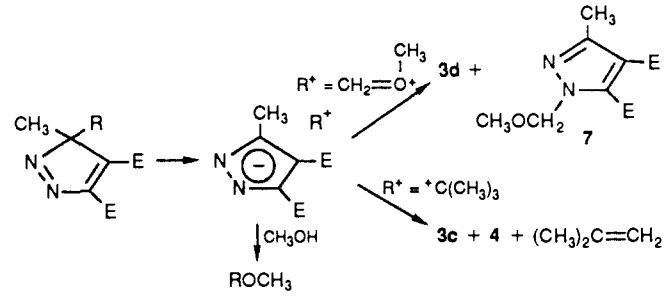


Rearrangements of heterocyclic cyclopentadiene-like ring systems are known also.[9]

All thermal rearrangements of that type are commonly described as suprafacial 1,5-sigmatropic rearrangements to denote a one-step mechanism in which the migrating group remains continuously and covalently bonded to the rest of the molecule as transfer from one ring atom to another proceeds.[2,10] We report examples of such rearrangements that require a two-step mechanism. The evidence for a discrete intermediate comes from substituent effects on rearrangement rates and from some unusual coproducts.

Compounds **1** (Scheme II) were prepared by in situ cycloaddition of the appropriate diazoalkanes to dimethyl acetylenedicarboxylate. The diazoalkanes were generated by photolysis of oxadiazolines.[11] Pyrazoles **1a** and **1b** were isolated before thermolysis in benzene at 160 °C (sealed tube) whereas **1c** and **1d** rearranged in the medium in which they were formed. Thermolysis of **1a** afforded **2a** (~83%), **3a** (~9%), and several minor products totaling 8%. Similar *normal* rearrangement of **1b** occurred to afford **2b** (67%) and **3b** (33%). Those processes can be understood in terms of competitive 1,5-sigmatropic alkyl rearrangements, to N to form **3** and to C to form an intermediate (**5**) that rearranges through **6** to **2** by sequential ester group migrations[12] (Scheme III). Ethyl must migrate faster than methyl (in **1b**), and the greater selectivity of ethyl in **1b**, over methyl in **1a**, for migration to N may reflect steric hindrance in the transition structure leading to **5**.[13]

Scheme IV



In contrast to the normal behavior of **1a** and **1b**, pyrazole **1c** afforded only **3c** (39%) and **4** (61%) plus isobutene (60%). Moreover, **1c** afforded those products at ambient temperatures (~20 °C) in solutions of **1c** prepared at ca. -20 °C,[11] indicating a greatly enhanced reactivity relative to those of **1a** and **1b**. Even more labile than **1c** was **1d**, an assumed intermediate that was not observable by ^1H NMR spectroscopy when 1-methoxy-2-diazopropane in toluene-d_8 was treated with dimethyl acetylenedicarboxylate in the temperature range -20 to -30 °C. What was observed instead was growth of the NMR signals of **3d**, the product of C to N migration of the methoxymethyl group of the transient **1d**.

Analogous reactions carried out in methanol or in methanol-d_4 were revealing. Again **1c** afforded **3c** (20%), **4** (80%), and isobutene (~5%). However, *tert*-butyl methyl ether (72%) was formed also. Similarly, **1d** when generated as a transient in CD_3OD afforded **3d** (29%), **4** (as D analogue, 71%), and $CD_3OCH_2OCH_3$ (39%). We were unable to detect the aromatic isomer of **3d** from reaction in methanol, but in $CDCl_3$ solvent, the products from **1d** were **3d** (70%) and isomer **7** (30%), Scheme IV.

The enormous rate enhancement[14] for rearrangement of **1c** and **1d**, the fact that **1d** forms both **3d** and **7** in $CDCl_3$, and the observation of substantial yields of solvolysis-type products in methanol solvent demand a change of mechanism from the normal concerted migration to a two-step process involving ion-pair formation in the first and rate-limiting step (Scheme IV). Presumably the stepwise rearrangement of **1** becomes important only in those cases where R^+ is a relatively stable cation and it represents part of a mechanistic continuum that runs from concerted with very little charge separation, through transition structures with considerable separation of charge,[15] to the two-step ion-pair extreme.

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(13) The situation may be complicated by reversibility (e.g., return of **5** to **1**), but another complication, the further clockwise migration of E in **5** to the other ring nitrogen, was rigorously excluded. X-ray crystal structures of **2a** and **2b** showed that those structures are indeed 1,3-diesters and not 1,5-diesters. Frampton, C.; Majchrzak, M. W.; Warkentin, J. *Can. J. Chem.*, submitted.

(14) Leigh and Arnold[9] have shown that 1,5-sigmatropic rearrangements of 3,4-diaryl-5,5-dimethyl-3*H*-pyrazoles have rate constants $\leq 30 \times 10^{-5}$ s^{-1} at 193.8 °C. We have been frustrated, thus far, in attempts to determine how fast **1d** rearranges, because the 1,3-dipolar cycloaddition by which it was prepared[11] becomes quite slow at temperatures below -20 °C. It is clear, however, that the rate constant for migration of the CH_2OCH_3 group must be at least 10^5 times as large as that of the closest primary model, the CH_2CH_3 group, given that **1d** rearranges fast below -20 °C whereas **1b** rearranges at 160 °C.

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A radical pair mechanism, like that which has been proposed[5c,d] to account for low stereochemical integrity in 1,5-alkyl group migrations, is a less likely explanation because α-alkoxyalkyl radicals are not greatly stabilized relative to their primary alkyl counterparts.[16] The corresponding cations, on the other hand, are hardly comparable, for the former are oxonium species rather than carbocations.

(16) In a model reaction that involves radical pair formation ($ArCH_2HgCH_2Ar \rightarrow ArCH_2^{\bullet} + {}^{\bullet}HgCH_2Ar$),[17] *p*-methoxy is not rate enhancing, within experimental error, relative to *p*-methyl and only 3.4-fold enhancing relative to *p*-H.

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Synthetic Flux-Promoting Compounds. Exceeding the Ion-Transporting Ability of Gramicidin

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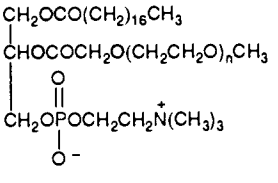
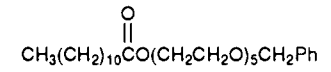
Discourses on membrane transport, such as this communication, often begin by extolling the importance of the subject. Continuing the practice, we note briefly that membrane transport underlies research into the molecular basis of diseases such as hypertension,[1] cancer,[2] epilepsy,[3] cystic fibrosis,[4] and malaria.[5] Our own specific interest in transport processes relates here to the synthesis of organic compounds that emulate the ion-channeling ability of gramicidin. Gramicidin is a pentadecapeptide antibiotic whose dimers from cation-conducting pores in lipid bilayers. So potent is gramicidin that a single channel carries a greater ion current than can an entire 1.0 × 1.0 mm gramicidin-free membrane.[6] To date only a few non-peptide mimics have been studied.[7-10] The examples reported herein are characterized by an attractive simplicity and a remarkable activity (surpassing gramicidin under certain conditions).

Discovery of our flux-promoting compounds was, admittedly, fortuitous. The original goal had been to synthesize and test phospholipids bearing a polyether chain (I). These materials proved incapable of accelerating ion movement across bilayers.



I

Such was not the case, however, with intermediates acquired in the synthesis of I having the general structure $RO(CH_2CH_2O)_nR'$. Upon discovering that these compounds facilitate ion translocation, we systematically varied the three sections of the molecules (R, *n*, and R') to optimize the effect. As will be shown, the greatest success was achieved with II where R = dodecanoyl, *n* = 5, and R' = benzyl.



II

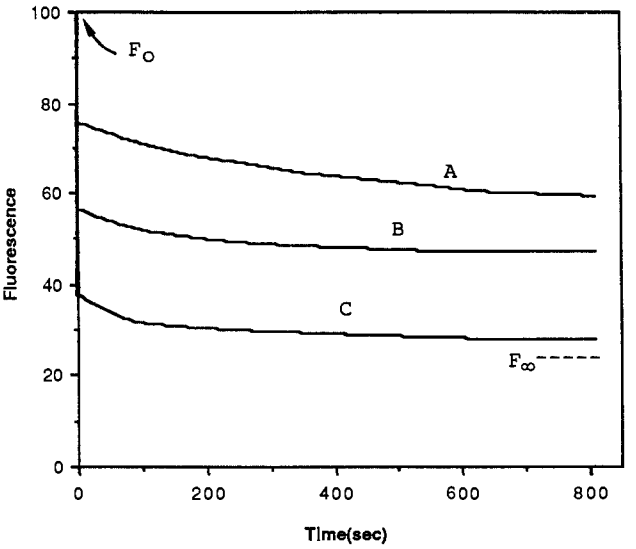


Figure 1. Fluorescence vs time data after adding HCl to pyranine-containing vesicles so as to abruptly lower the external pH from 7.7 to 6.6 (K_2HPO_4 buffer, 20.0 °C, [DSPC] = 0.3 mM). Polyether additives are all present at 45 molecules/vesicle assuming 5000 lipids/vesicle. Curve A represents plot for blank (no additive) as well as three inactive polyethers: (a) $R_1 = R_2$ = dodecanoyl, n = 5; (b) $R_1 = R_2$ = benzyl, n = 5; (c) R_1 = hexanoyl, R_2 = benzyl, n = 5. Curve B: R_1 = dodecanoyl, R_2 = benzyl, n = 3. Curve C: compound II.

Ion flux was monitored by a simple method that Kano and Fendler[11] developed a decade ago. Thus, 0.3 mM distearoylphosphatidylcholine (DSPC) and an acid-responsive fluorescent dye (the tetraanion of 8-hydroxy-1,3,6-pyrenetrisulfonic acid) were cosonicated[12] at 60 °C in a weak pH = 7.7 buffer containing 0.1 M KCl. This created unilamellar vesicles (diameter = 30 ± 5 nm according to our QELS measurements)[13] with dye situated both in the enclosed volume and in the bulk water. The latter was readily removed by gel filtration through a Sephadex G-25-80 column. A flux-promoting compound (gramicidin D or one or our mimics) was then added at the micromolar level and allowed to equilibrate at 20.0 °C with the vesicles. When an HCl pulse lowered the bulk pH from 7.7 to 6.6, protons entered the vesicles, dye with its pK_a = 7.2 became protonated, and the fluorescence was thereby depleted. Note that the dye, being polyanionic, cannot escape the vesicles,[11] nor will the dye bind to the membrane walls since all bilayers were provided with 10% anionic distearoylphosphatidate.[13]

Plot C in Figure 1 shows the fluorescence vs time dependence when there are only 45 molecules of II/"5000-DSPC" vesicle. It is seen that the fluorescence drops precipitously from an initial value of F_0 = 100% to a value somewhat greater than the theoretical F_∞ = 24%. This can be explained in a manner totally consistent with the literature[14-16] by assuming the following: (a) Any vesicle with even a single functional channel suffers an instantaneous and electrically neutral ion flux. (b) A certain number of vesicles lack a channel at the concentrations of the experiment. Increasing the concentration of II to roughly 75 molecules/vesicle

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