

the salophene moiety, and hydrogen bonding between the NH₂ functions of urea and the oxygens of the ethylene glycol bridge of the host. However, these compounds are only poorly soluble in most solvents. Therefore these receptors were further modified by replacing the benzene ring of the salophene by a 1,2-cyclohexyl moiety to obtain more soluble receptors (1-4).¹⁸ Compounds 1-4 were prepared from the corresponding dialdehydes and *cis*-1,2-cyclohexanediamine in methanol according to the route outlined for the corresponding salophene metallomacrocycles in ref 17 (see Figure 1).

These compounds have been used as carriers in a supported liquid membrane composed of a porous polymeric support (Accurel) impregnated with *o*-nitrophenyl *n*-octyl ether (NPOE)^{4,6,7} to investigate the relation between the ring size of the metallomacrocyclic and the rate of urea transport.¹⁹ Since the partition of these carriers might still be rather low, crown ether salophene derivatives have been modified with a binaphthyl (5) or a calix[4]arene (6) function to obtain a lipophilic and selective urea carrier. Compounds 5 and 6 were prepared from the corresponding dialdehydes and 1,2-benzenediamine in THF according to ref 17.²⁰

Table I shows that the urea fluxes using the cyclohexyl receptors (1-4) depend strongly on the ring size of these carriers. Compound 1 results in a urea flux (2.3×10^{-8} mol cm⁻² h⁻¹) that is comparable to the blank flux observed in experiments where no carrier is used (1.6×10^{-8} mol cm⁻² h⁻¹), while the larger rings transport urea much better, especially compound 2 ($n = 3$). With this compound the urea flux (20.6×10^{-8} mol cm⁻² h⁻¹) is 13 times higher than the blank flux and also higher than fluxes obtained by using comparable concentrations of compounds 1 (2.3×10^{-8} mol cm⁻² h⁻¹) and 3 (8.4×10^{-8} mol cm⁻² h⁻¹).²⁴ Compound 4 is only poorly soluble in NPOE and results also in a lower flux (5.9×10^{-8} mol cm⁻² h⁻¹ when a 2.8 mM solution is used compared to 12.0×10^{-8} mol cm⁻² h⁻¹ when the same concentration of 2 is used). The different rates of transport are in agreement with CPK models, which show that compound 1 has a cavity that is too small to complex urea and which show the best fit for compound 2 (see Figure 2 for the X-ray crystal structure).¹⁸

Table I also shows that, upon replacement of the receiving aqueous phase one and two times respectively, the flux for the cyclohexyl carrier 2 decreases from 20.6 to 10.8 and 6.8×10^{-8} mol cm⁻² h⁻¹. This means that the carrier leaches out to the aqueous phases. This is not observed for the binaphthyl 5 or calix[4]arene 6 modified carriers. In these cases the urea fluxes (22.2×10^{-8} mol cm⁻² h⁻¹ for 5 and 20.0×10^{-8} mol cm⁻² h⁻¹ for 6) are comparable to those obtained with carrier 2 but do not decrease upon replacement of the receiving aqueous phase, so that when more lipophilic carriers are used, a stable membrane is obtained.

In summary: neutral molecules like urea can be transported by macrocyclic carriers through supported liquid membranes. High fluxes can be obtained by using carriers that possess a cavity in which the guest molecule fits well. The membrane stability can be much improved by using carriers modified with lipophilic groups like binaphthyl or calixarene units. In the future the

transport selectivity for urea will be studied by competition experiments. A transport model which was previously developed for cation transport^{4,6,7} can be modified to describe the transport of neutral molecules.

Acknowledgment. We thank the Koninklijke/Shell Laboratorium Amsterdam for their financial support.

A Simple, Effective Method for Achieving High 1,4-Relative Asymmetric Induction in Carbonyl Addition Reactions

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Received December 24, 1990

One of the most challenging problems in practical organic synthesis is the stereocontrolled installation of new stereogenic centers at sites far removed from existing stereocenters in acyclic molecules.² Herein we report a unique approach to 1,4-relative asymmetric induction in which neighboring-group participation³ is postulated as the foundation for high levels of remote asymmetric induction (Scheme 1).

In initial studies testing this hypothesis, the combination of trimethylsilyl cyanide (TMSCN) as the nucleophile and trimethylsilyl trifluoromethanesulfonate (TMSOTf)⁴ as the Lewis acid catalyst was chosen for investigation in conjunction with acetal electrophiles. When dimethoxy acetals were utilized as substrates, disappointingly low diastereoselectivities were observed (Table I, entry 1).⁵ Because the nature of the acetal was expected to be an important factor in determining the diastereoselectivity for

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(19) The urea transport was monitored by UV analysis of the complex formed between urea and *p*-(dimethylamino)benzaldehyde at 435 nm, following literature procedures.²¹⁻²³

(20) To be published.

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(24) The carrier-mediated urea flux can be expressed as

$$J = \frac{D_m K_{ex} [U]_w^0 [C]_m^0}{d(P + Q K_{ex} [U]_w^0)}$$

in which D_m = diffusion coefficient of the complex, K_{ex} = extraction coefficient, $[U]_w^0$ = initial urea concentration in the source phase, $[C]_m^0$ = initial carrier concentration in the membrane, d = membrane thickness, $P = 1 + V_r V_m^{-1} K_c^{-1} + V_s V_m^{-1} K_c^{-1}$, $Q = 1 + V_r V_m^{-1} K_c^{-1} + K_w V_s V_m^{-1} K_c^{-1} K_{ex}^{-1}$, V_r = volume receiving phase, V_s = volume source phase, V_m = membrane volume, K_c = partition coefficient of the carrier, and K_w = association constant in water. Substantiation of this model will be the subject of a future publication.

Scheme I

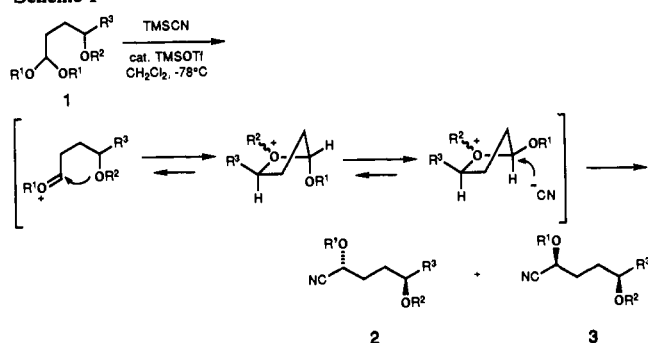


Table I. 1,4-Relative Asymmetric Induction in the Reaction of TMSCN with Alkoxy Acetals (1) in the Presence of Catalytic TMSOTf^a

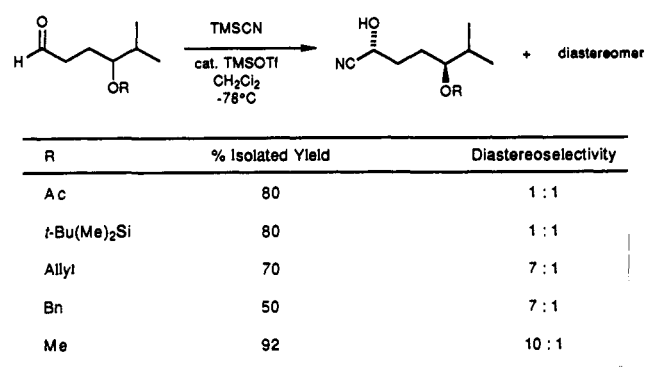
entry	R ¹	R ²	R ³	% isolated yield ^b (2 + 3)	diastereo-selectivity ^c (2:3)
1	Me	Me	Me	95	1.5:1
2	<i>i</i> -Pr	Me	Me	96	5:1
3	<i>i</i> -Pr	Me	<i>n</i> -Bu	95	5:1
4	<i>i</i> -Pr	Me	<i>t</i> -Bu	95	6:1
5	<i>i</i> -Pr	Me	Ph	93	6:1 ^d
6	<i>i</i> -Pr	Me	<i>i</i> -Pr	97	15:1
7	<i>i</i> -Pr	Me	C ₆ H ₁₁	100	10:1
8	CICH ₂ - CHCH ₂ Cl	Me	<i>i</i> -Pr	89	11:1 ^d
9	Bn	Me	<i>i</i> -Pr	94	8:1
10	Bn	Bn	<i>i</i> -Pr	95	6:1

^aReactions were performed in CH₂Cl₂ at -78 °C with 1 equiv of TMSCN and 10 mol % TMSOTf unless otherwise noted. ^bRefers to yields of purified material. All of these compounds have been fully characterized spectroscopically (¹H NMR, ¹³C NMR, IR), and elemental composition has been established by high-resolution mass spectrometry and/or combustion analysis. ^cDetermined on the crude reaction mixture by fused silica capillary gas chromatography. ^dStannic chloride was utilized as the Lewis acid.

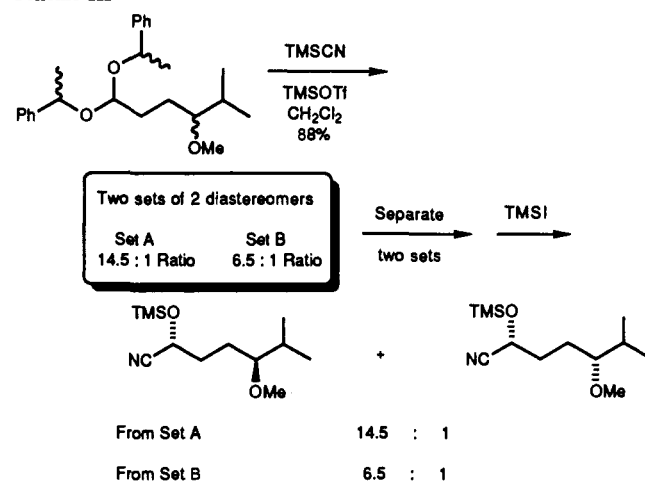
the processes under study,⁶ more sterically imposing diisopropoxy acetals were utilized (Table I, entries 2–8). In fact, excellent diastereoselectivities were observed in these cases. Unfortunately, the ultimate generation of an isopropyl ether leaves one with little flexibility in terms of conversion to useful organic products. Gratifyingly, we have found that acetals derived from benzyl alcohol can be utilized in the reaction, albeit with some concession to diastereoselectivity (entry 9).⁷ Because the resulting benzyl alcohols can be readily cleaved under a variety of reaction conditions, this protocol represents a viable means to accomplish the desired conversions.

Several experiments were also performed on aldehyde electrophiles wherein the stereodirecting substituent was altered (Scheme II). These studies have lent credence to the postulate that participation may be responsible for the diastereoselectivity. Neither acetoxy substituents nor *tert*-butyldimethylsilyloxy groups were expected to be effective participants in the processes proposed,⁸ and indeed reactions employing these substituents were

Scheme II



Scheme III



stereorandom. On the other hand methoxy, benzyloxy, and allyloxy substituents can all be envisioned as effective participants, and transformations involving these groups at the stereodirecting center demonstrated marked diastereoselection.

An interesting example of double asymmetric induction has also been realized in this study (Scheme III). Thus, when 1,1-bis[(α -methylbenzyl)oxy]-4-methoxy-5-methylhexane was treated with TMSCN/TMSOTf under the standard reaction conditions, a mixture of four diastereomers was generated. Two of these diastereomers (set A, 14.5:1 ratio) could readily be separated from a second set of two diastereomers (set B, 6.5:1 ratio). After separation of these two sets (which were generated in equal quantities), the mixtures were treated with TMSI, cleaving the (α -methylbenzyl)oxy protecting groups. The same ratios of diastereomers were found in these cleavage products as were present in the two original sets of diastereomers A and B, indicating that sets A and B were epimeric at the (α -methylbenzyl)oxy group and that the stereogenic center in that substituent contributed in a manner that led to a matched and mismatched pair of diastereomeric transition states.⁹

The diastereoselectivities recorded herein are among the highest 1,4-relative asymmetric inductions yet reported for carbonyl addition and related reactions. Another novel concept embodied within this work is the absence of a metal template for stereochemical control in these transformations. Freed from the constraints of chelation control as a construct to achieve high

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diastereoselectivity, one can envision simple solutions to a wide range of stereochemical transformations that are currently deemed difficult to accomplish. We are actively pursuing a variety of these. Finally, application of a unique double asymmetric induction phenomenon provides an inroad to even higher diastereoselectivities in nucleophilic addition reactions to carbonyl substrates.

Acknowledgment. We thank the National Science Foundation for their generous support of our program.

Supplementary Material Available: Complete experimental details for all reactions reported, as well as ^1H and ^{13}C NMR spectra for all compounds (34 pages). Ordering information is given on any current masthead page.

Two Rhenium Complexes That Contain an Unsupported Metal-Metal Double Bond in the Presence of Potentially Bridging Ligands

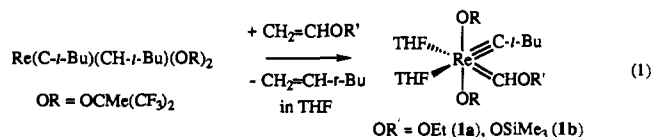
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It is not obvious why complexes that contain an unsupported metal-metal double bond (i.e., no bridging ligands) should be so rare, while there are scores of examples of complexes that contain unbridged metal-metal single bonds, or (for molybdenum, tungsten, and rhenium) unbridged triple or quadruple bonds.¹ Two types of complexes that contain an unsupported metal-metal double bond have been reported, $(\text{Me}_3\text{SiCH}_2)_3(\text{O})\text{Re}(\mu\text{-O})[\text{Re}(\text{PMe}_3)_4]\text{Re}(\text{O})_2(\text{CH}_2\text{SiMe}_3)_2$ and macrocycle complexes such as $[\text{M}(\text{octaethylporphyrin})]_2$ ($\text{M} = \text{Ru}, \text{Os}$)³ and $[\text{Ru}(\text{C}_{22}\text{H}_{22}\text{-N}_4)]_2$.⁴ In neither type is there an opportunity for ligands to bridge the metal-metal double bond. We report here the synthesis and structural determination of two complexes that contain an unsupported rhenium-rhenium double bond in the presence of potentially bridging ligands. To our knowledge these are the first such complexes to be synthesized.

Vinyl ethers react smoothly at room temperature in tetrahydrofuran with *syn*- $\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})[\text{OCMe}(\text{CF}_3)_2]_2$,^{5,6} to afford **1a**⁷ and **1b** quantitatively (eq 1). These species rapidly



exchange tetrahydrofuran at room temperature and are the only reported examples of heteroatom-substituted high oxidation state alkylidene complexes. When analogous reactions in C_6D_6 or CD_2Cl_2 are followed by proton NMR analysis, the base-free

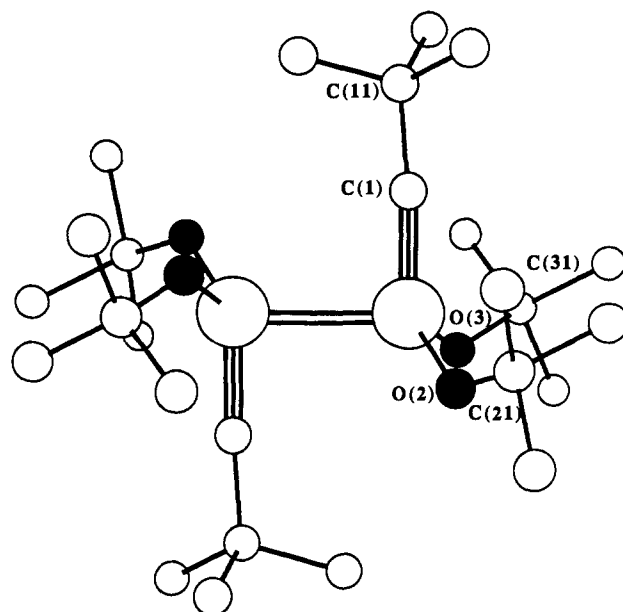
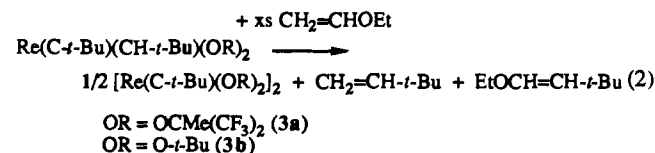


Figure 1. A drawing of the molecular structure of $[\text{Re}(\text{C-}t\text{-Bu})(\text{O-}t\text{-Bu})_2]_2$ (**3b**).

Table I. Selected Bond Distances (Å) and Angles (deg) in **3a** and **3b**

	3a	3b
Re-Re*	2.3836 (8)	2.396 (1)
Re-C(1)	1.728 (8)	1.721 (7)
Re-O(2)	1.925 (5)	1.901 (5)
Re-O(3)	1.932 (5)	1.909 (4)
O(2)-C(21)	1.395 (9)	1.421 (7)
O(3)-C(31)	1.383 (9)	1.425 (8)
Re-Re*-C(1)	90.0 (2)	89.5 (2)
Re-C(1)-C(11)	177.7 (6)	175.6 (5)
Re-O(2)-C(21)	136.9 (5)	135.9 (4)
Re-O(3)-C(31)	140.5 (5)	135.9 (4)
O(2)-Re-O(3)	117.8 (2)	115.1 (2)
O(2)-Re-C(1)	112.8 (3)	114.9 (3)
O(3)-Re-C(1)	113.6 (3)	113.8 (3)

complexes, $\text{Re}(\text{C-}t\text{-Bu})(\text{CHOR}')[\text{OCMe}(\text{CF}_3)_2]_2$ [$\text{OR}' = \text{OEt}$ (**2a**), OSiMe_3 (**2b**)], are observed as a mixture of *syn* and *anti* rotamers, the *syn*/*anti* ratio varying with reaction conditions and rotameric purity of the starting material. These species decompose if their solutions are concentrated. $\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{O-}t\text{-Bu})_2$ ⁸ reacts slowly with ethyl vinyl ether in dichloromethane over the course of 2 days to give dark red prisms of $[\text{Re}(\text{C-}t\text{-Bu})(\text{O-}t\text{-Bu})_2]_2$ (**3b**)⁹ in 50-60% isolated yield, *cis*- and *trans*-3,3-dimethylbutenyl ethyl ether,^{10a,b} and neohexene (eq 2).^{10c} Con-



centrated solutions of crude **2a** in dichloromethane, pentane, or toluene decompose in minutes at room temperature to give

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(6) *Syn* refers to the rotamer in which the alkylidene substituent points toward the neopentylidene ligand.

(7) Synthetic procedures, NMR data, and analytical data are available as supplementary material. *syn-1a* and *syn-1b* isomerize to mixtures of *syn* and *anti* rotamers in solution. The structural type shown for **1a** and **1b** is only one of two possibilities, the other being a complex containing *cis* OR ligands.

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(9) The analogous neophylidene complex, $[\text{Re}(\text{CCMe}_2\text{Ph})(\text{O-}t\text{-Bu})_2]_2$ (**3c**), also has been prepared. (See supplementary material.)

(10) (a) Identified by ^1H NMR comparison with samples prepared via Wittig-like reactions involving tantalum alkylidene complexes.^{10b} (b) Schrock, R. R. *J. Am. Chem. Soc.* **1976**, *98*, 5399. (c) Neohexene is formed via metathesis of the vinyl ether with the starting neopentylidene complex as in eq 1. Dimethylbutenyl ethyl ether is apparently formed from reaction of $\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR})_2$ with **2a** or **3a** as there is not further formation of this olefin once the neopentylidene complex has been consumed. The ratios of product olefins are dependent on the reaction conditions.