

Ligand Intermediates in Metal-Catalyzed Reactions

Annual Technical Report

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research period summarized in report: 9/1/90-8/31/91

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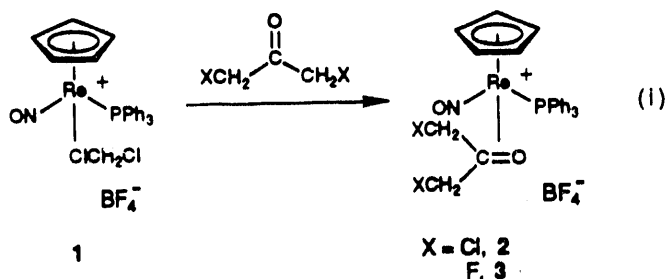
I. RESEARCH PROGRESS

This has been an extremely productive project period. Six new papers have appeared in print or been accepted for publication since the previous report (A9-14). Principal achievements are as follows.

A. π/σ Equilibria in Aldehyde and Ketone Complexes (pub. A-8, A-11)

Aldehyde and ketone complexes are intermediates in many metal-catalyzed reactions. We have sought to define the factors that affect the thermodynamics of π/σ binding, and differences in reactivity of the two binding modes. In the previous report, we described fifteen aromatic aldehyde complexes of the formula $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{O}=\text{CHAr})]^+ \text{BF}_4^-$. IR analyses (CH_2Cl_2) showed these to be >96:<4 to 15:85 mixtures of π/σ isomers (ν_{NO} : π 1745-1733; σ 1701-1692 cm^{-1}). Electron withdrawing substituents (which enhance aldehyde π acidity and lower σ basicity) favor the π binding mode, while electron donating substituents have an opposite effect.

We wondered whether parallel electronic effects might be observable in ketone complexes. Methyl ketone complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\eta^1\text{-O}=\text{C}(\text{CH}_3)\text{R})]^+ \text{X}^-$ exist exclusively as σ isomers. Thus, we sought to prepare analogs with electron-withdrawing ketone substituents. Accordingly, reactions of dichloromethane complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{ClCH}_2\text{Cl})]^+ \text{BF}_4^-$ (1) with 1,3-dichloroacetone and 1,3-difluoroacetone gave the π complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\eta^2\text{-O}=\text{C}(\text{CH}_2\text{X})_2)]^+ \text{BF}_4^-$ (X = 2, Cl; 3, F), as shown in eq 1. Both IR and NMR spectra showed no sign of any σ isomers. A crystal structure of 3 (Figure 1; PF_6^- salt) verified the π binding mode in the solid state.



MASTER

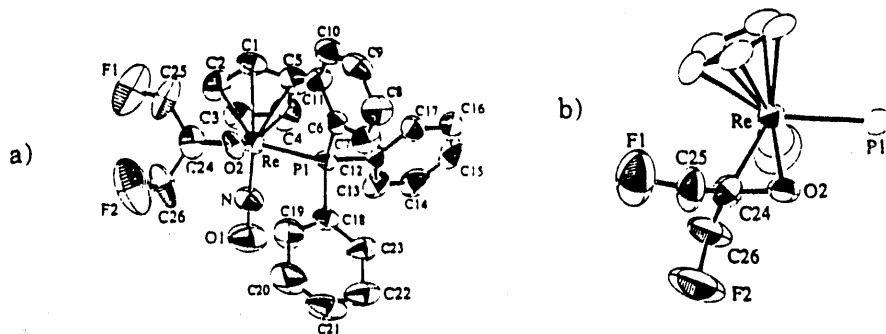
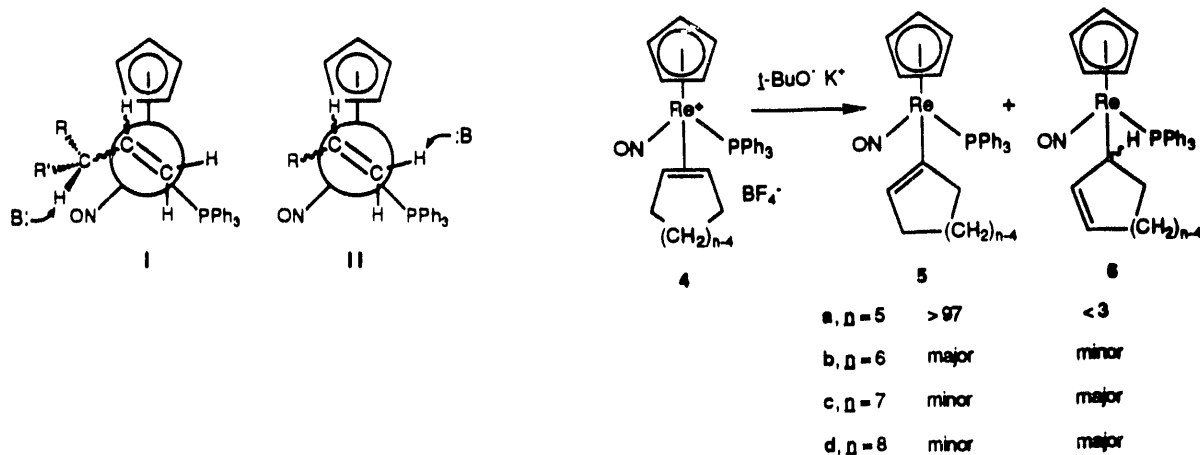


Fig. 1. Views of the cation of difluoroacetone complex $(\{\eta^5\text{-C}_6\text{H}_4\}\text{Re}(\text{NOXPPH}_3)(\eta^2\text{-O}=\text{C}(\text{CH}_2\text{F})_2\})^+ \text{PF}_6^- (3^+ \text{PF}_6^-)$: (a) numbering diagram; (b) view down rhenium-nitrogen bond with phenyl groups omitted. Selected bond lengths (Å) and angles ($^\circ$): Re-C24 2.17(1), Re-O2 2.044(6), C24-O2 1.35(1), Re-N 1.737(9), Re-P 2.449(3), N-O1 1.19(1), O2-Re-C24 37.1(3), Re-O2-C24 76.5(5), Re-C24-O2 66.4(5), Re-N-O1 173(1), N-Re-P 90.5(3).

B. A New Carbon-Hydrogen Bond Activation Process: Abstraction of Vinylic Protons from Alkene Complexes (pub. A-10)

Many cationic alkene complexes $[\text{L}_n\text{M}(\text{H}_2\text{C}=\text{CHCH}_2\text{R})]^+$ undergo allylic deprotonation when treated with mild bases, as shown in I. However, in our previous report we described a facile, unprecedented alternative vinylic deprotonation mode (II) that provides a new alkene carbon-hydrogen bond activation protocol. We have extended these studies to the cycloalkene complexes 4 shown in Scheme I.

Scheme I. Summary of Products from the Reactions of Cycloalkene Complexes 4 and $t\text{-BuO}^- \text{K}^+$ in THF.



In an attempt to better understand this selectivity, the cyclopentene complex 4a was studied in detail. First, the cyclopentylidene complex 7 was independently prepared as shown in Scheme II, and characterized crystallographically. Its independent stability excludes any intermediacy in the deprotonation of 4a. Second, a crystal structure of the methylcyclopentadienyl analog of 4a was executed, and all hydrogens were located. Based upon the structures shown

in Figure 2, there would appear to be no intrinsic stereoelectronic problem associated with allylic proton abstraction.

Scheme II. Vinylic Deprotonation of Cyclopentene Complex 4a, and Synthesis of Cyclopentadiene Complex 7.

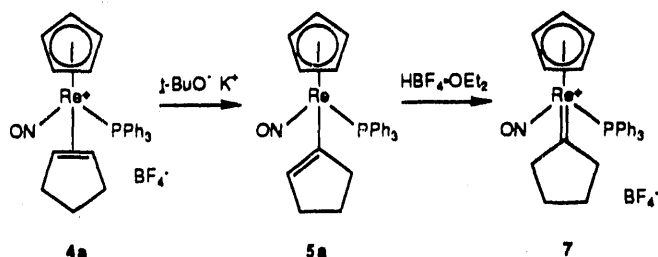
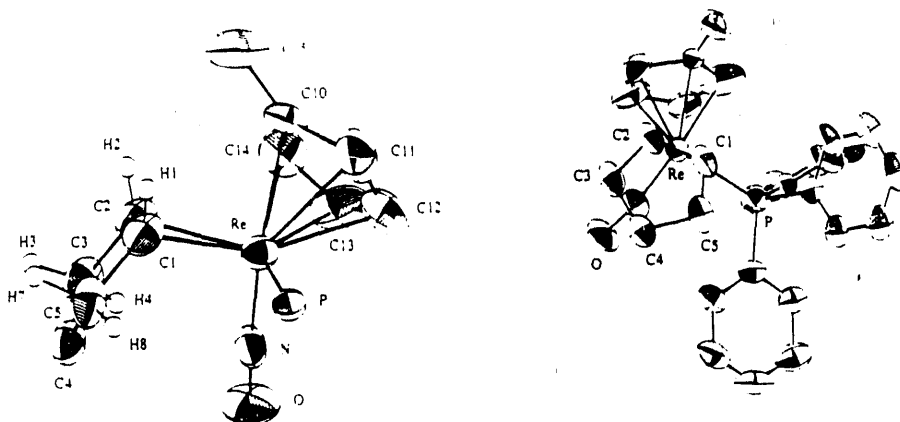


Figure 2. Views of a methylcyclopentadienyl derivative of cyclopentene complex 4a.

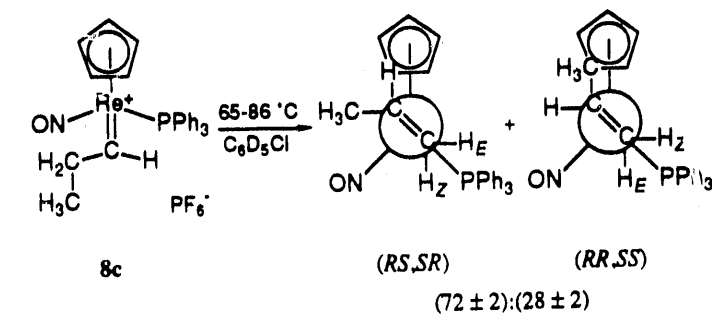


C. Mechanism of Rearrangement of Alkylidene to Alkene Complexes (pub. A-13)

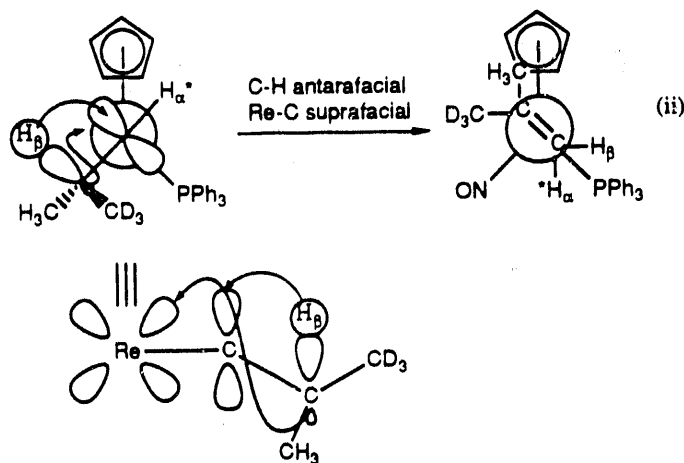
Many cationic alkylidene complexes, $[L_nM(=CRCHR'')]^+$, have been found to undergo 1,2-hydride migrations to cationic alkene complexes $[L_nM(RHC=CR'R'')]^+$. We have completed the first detailed mechanistic study of these carbon-hydrogen bond activation processes. Rhenium alkylidene complexes of the formula $[(\eta^5-C_5H_5)Re(NO)(PPh_3)(=CRCHR'')]^+ X^-$ (8) have been employed, as exemplified in Scheme III.

Key features include: (1) modest primary kinetic isotope effects, (2) substantial inverse secondary deuterium isotope effects ($k_{Re=CH}/k_{Re=CD}$), (3) retention of configuration at rhenium, (4) intramolecular hydride migration and lack of PPh₃ dissociation, and (5) high stereoselectivity at the migration origin and terminus for certain substrates. Substituent effects suggest strong parallels to Wagner-Meerwein rearrangements. However, the transition state

Scheme III. Thermolyses of propylidene complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{=CHCH}_2\text{CH}_3)]^+ \text{PF}_6^-$ **8c** and deuterated derivatives.



deuterium in reactant	deuterium in H_Z , H_E of product	
D_α ($\text{Re}=\text{CDCH}_2\text{CH}_3$)	$40 \pm 3\% \text{ H}_Z$ $60 \pm 3\% \text{ H}_E$	$44 \pm 3\% \text{ H}_Z$ $56 \pm 3\% \text{ H}_E$
2 D_β ($\text{Re}=\text{CHCD}_2\text{CH}_3$)	$53 \pm 3\% \text{ H}_Z$ $47 \pm 3\% \text{ H}_E$	$40 \pm 3\% \text{ H}_Z$ $60 \pm 3\% \text{ H}_E$



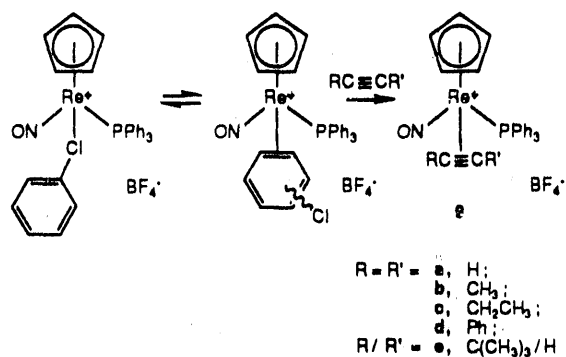
formally involves four electrons, and the symmetry-allowed mechanism shown in eq ii has been proposed.

D. Rearrangement of Terminal Acetylene to Vinylidene Complexes (pub. A-9)

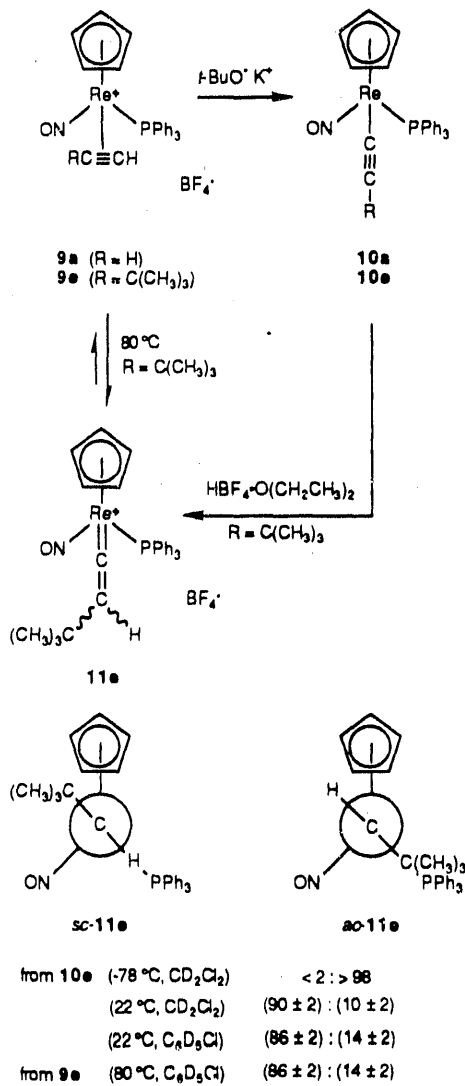
We find that alkyne complexes of the formula $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{RC}\equiv\text{CR}')]^+ \text{BF}_4^-$ (**9**) are readily prepared as shown in Scheme IV. We have studied two types of carbon-hydrogen bond activation processes of the terminal alkyne complexes **9a,e**. First, reactions with $\text{t-BuO}^- \text{K}^+$ give the corresponding terminal acetylide complexes $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{C}\equiv\text{CR})$ (**10a,e**) as shown in Scheme V. These transformations are reminiscent of the vinylic deprotonations in Schemes I and II.

Second, the bulky t -butyl acetylene complex **9e** undergoes a prototropic re-

Scheme IV. Synthesis of Alkyne Complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{RC}\equiv\text{CR}')]\text{BF}_4^-$ (**9**).



Scheme V. Reactions of Terminal Alkyne Complexes 9a, e.



arrangement at 80 °C to give the *t*-butyl vinylidene complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})\text{-}(\text{PPh}_3)(=\text{C}=\text{CHC}(\text{CH}_3)_3)]^+ \text{BF}_4^-$ (11e; Scheme V). The parent acetylene complex 9a shows no tendency to isomerize, suggesting a steric driving force. Further, isomerization ceases when a 84:14 11e/9e ratio is attained. An identical mixture can be generated by protonation of acetylide complex 10e with $\text{HBF}_4 \cdot \text{OEt}_2$ (Scheme V). This clearly shows that terminal acetylene and vinylidene complexes are in equilibrium.

E. Synthesis and Reactivity of Lithiocarbide Complexes (pub. A-14)

It is well known that organic terminal acetylenes, $\text{RC}\equiv\text{CH}$, are easily deprotonated by strong bases ($\text{p}K_{\text{BH}^+} \geq 25$). Thus, we sought to investigate the acid/base chemistry of the terminal acetylide complex 10a. Deprotonation by an alkali metal base, $\text{M}^+ \text{B}^-$, would afford the first example of a transition metal/alkali metal carbide complex. Such compounds should in turn be potentially valuable precursors to other unusual bimetallic C_x complexes.

In order to facilitate the analysis of trapping experiments, authentic samples of methylated derivatives of 10a were desired. These were prepared as sketched in Scheme VI, and a variety of deprotonation/methylation conditions were investigated. In particular, the formation of methylacetylide complexes 12 and 14 was taken (together with supporting ^{31}P NMR data) as evidence for the intermediacy of lithiocarbide complexes $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{C}\equiv\text{CLi})$ (15) and $(\eta^5\text{-C}_5\text{H}_4\text{Li})\text{Re}(\text{NO})(\text{PPh}_3)(\text{C}\equiv\text{CLi})$ (16) (Scheme VII).

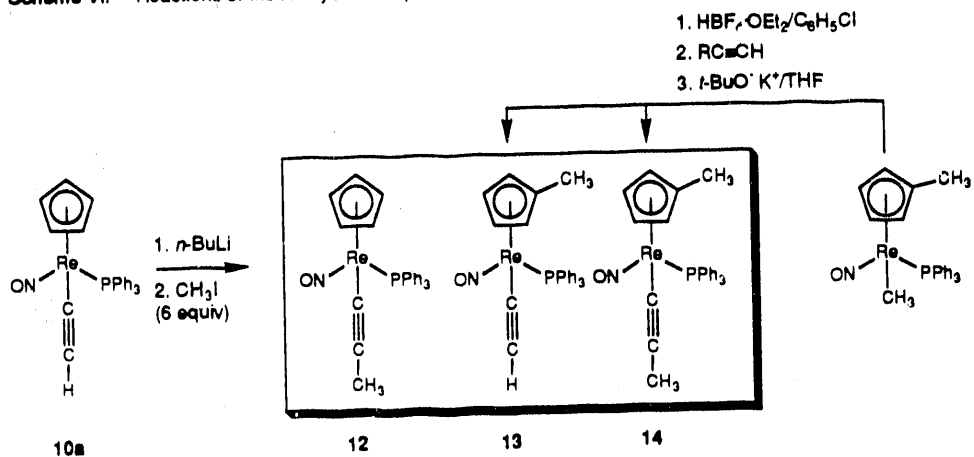
Since metal C_2 complexes are of particular current interest, we sought to convert 16 to an isolable heterobimetallic derivative. Thus, 10a, *n*-BuLi, and Ph_3SnCl (2.6 equiv) were reacted in a protocol analogous to Scheme VI, entry 5. Workup gave the bis(stannylated) complex $(\eta^5\text{-C}_5\text{H}_4\text{SnPh}_3)\text{Re}(\text{NO})(\text{PPh}_3)(\text{C}\equiv\text{CSnPh}_3)$ (17; Scheme VII) in 49% yield. Extensions of this methodology are currently under investigation.

F. New Catalysts for the Epimerization of Secondary Alcohols; Carbon-Hydrogen Bond Activation in Alkoxide Complexes (pub A-12, B-16)

We have discovered that secondary alcohols epimerize to mixtures of diastereomers in aromatic hydrocarbons at 65-90 °C in the presence of 10 mol% $(\eta^5\text{-C}_5\text{R}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{OCH}_3)$ (18; R = H, Me). Data are summarized in Chart 1. We have studied the mechanism of this previously undetected (for homogeneous, low-oxidation state metal complexes) carbon-hydrogen bond activation in detail.

The methoxide ligand of 18 first exchanges with the alcohol substrate to give alkoxide complexes $(\eta^5\text{-C}_5\text{R}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{OCHR}'\text{R}'')$ (19). Authentic samples

Scheme VI. Reactions of the Acetylide Complex 10a and *n*-BuLi.



Entry	<i>n</i> -BuLi	CH ₃ I addn.	Yield	Product Distribution (%)			
				10a	12	13	14
1 ^a	1.0 equiv. -80 °C, 1.5 h	0 °C	79%	8	66	0	26
2 ^a	1.5 equiv. -80 °C, 1.5 h	0 °C	89%	0	46	0	54
3 ^a	2.0 equiv. -80 °C, 1.5 h	0 °C	91%	0	0	0	100
4 ^b	1.0 equiv. 20 °C, 3 min	20 °C	71%	10	80	0	10
5 ^b	2.0 equiv. 20 °C, 3 min	20 °C	53%	0	8	0	92

^aSolvent THF. ^bSolvent 1:1 THF:Hexane.

Scheme VII. Lithiocarbide and Stannylcarbide Complexes

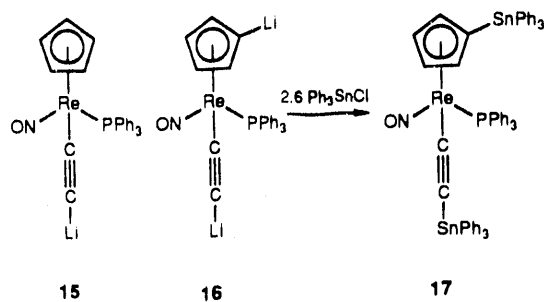
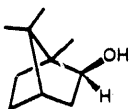
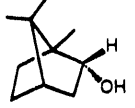
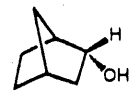
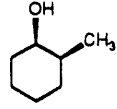
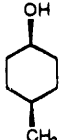
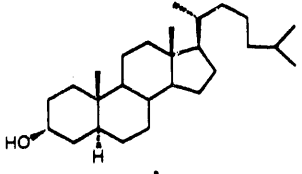
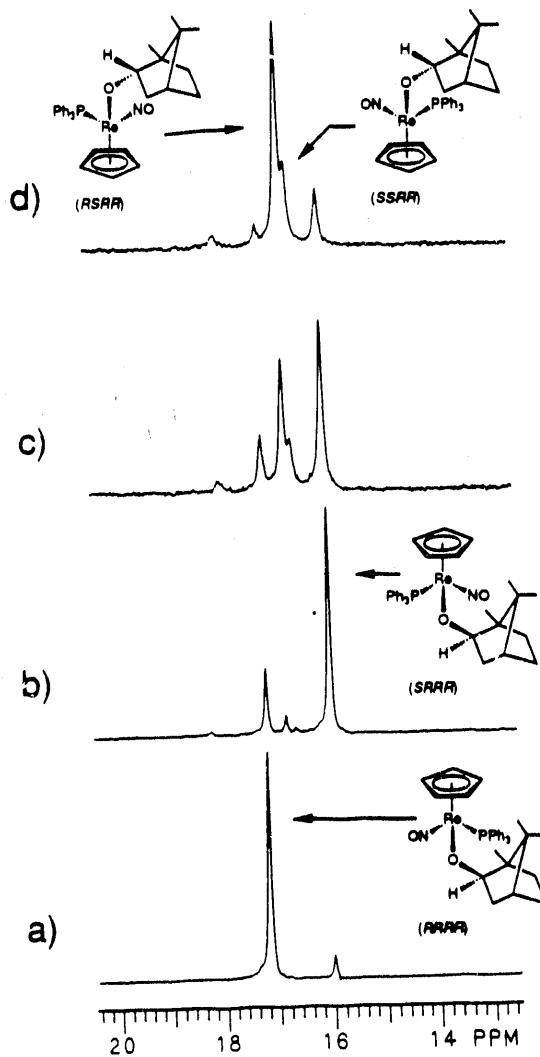


Chart 1. Data on the Epimerization of Secondary Alcohols by 10 mol % (η^5 -C₅R₅)Re(NO)(PPh₃)(OCH₃)

Starting Alcohol	Catalyst	Temp (°C)	Time (h)	Reactant : Product	$k_1 \times 10^5$ (s ⁻¹)	$k_2 \times 10^5$ (s ⁻¹)
 ((±)-exo-borneol) ^a				(exo/endo)		
	18	65	48	32:68	2.7 ± 0.2	1.3 ± 0.2
	18	65	48	32:68	2.2 ± 0.2	1.1 ± 0.2
	18-Me ₅	65	48	30:70	14 ± 1	5 ± 1
 ((±)-endo-borneol) ^a	18	65	48	68:32	1.2 ± 0.1	2.5 ± 0.1
				(endo/exo)		
 ((±)-endo-norborneol) ^a	18	71	180	24:76	0.52 ± 0.01	0.16 ± 0.01
	18	71		24:76	0.63 ± 0.01	0.20 ± 0.01
	18-Me ₅	71	162	18:82	1.03 ± 0.04	0.22 ± 0.04
 ((±)-cis-2-methylcyclohexanol) ^a				(cis/trans)		
	18	80	80	30:70	0.51 ± 0.03	0.21 ± 0.03
	18	80		28:72	0.51 ± 0.03	0.20 ± 0.03
	18-Me ₅	80	52	23:77	0.91 ± 0.04	0.27 ± 0.04
 (cis-4-methylcyclohexanol) ^b				(cis/trans)		
	18	91	40	28:72	1.5 ± 0.1	0.6 ± 0.1
	18	91		30:70	1.1 ± 0.1	0.5 ± 0.1
	18-Me ₅	93	14	30:70	3.9 ± 0.1	1.7 ± 0.1
 ((+)-α-cholestanol) ^a				(α/β)		
	18	80	48	28:72	1.2 ± 0.1	0.5 ± 0.1
	18	80		28:72	1.0 ± 0.1	0.4 ± 0.1
	18-Me ₅	80	48	30:70	1.9 ± 0.1	0.8 ± 0.1

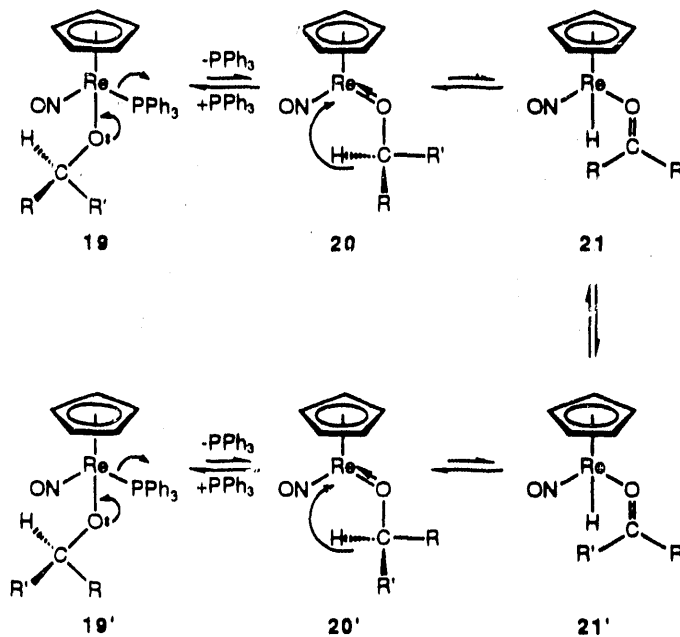
(a) In C₆D₆. (b) In C₆D₅CD₃.

Figure 3. Epimerization of (*RRRR*)-**19a**: (a) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of starting material at 35 °C; (b) spectrum after 9 h at 35 °C; (c-d) spectra after 0.6 and 10 h at 65 °C.



of diastereomerically and enantiomerically pure **19** have been prepared, where OCHR'R'' is derived from (+)- and (-)-, *exo*- and *endo*-borneol. NMR data show that epimerization occurs first at rhenium (ca. 35 °C) and then carbon (ca. 65 °C), as illustrated in Figure 3. Substitution reactions and rate experiments show that PPh₃ initially dissociates from **19** with anchimeric assistance by alkoxide oxygen lone pairs, as sketched in Scheme VIII. An intermediate with a trigonal planar rhenium (**20**), which can either return to **19** (with epimerization at rhenium) or undergo β-hydride elimination to the ketone hydride complex **21** (leading to epimerization at carbon), forms. Accordingly, rates of epimerization at carbon (but not rhenium) are strongly inhibited by added PPh₃, and show a significant k_H/k_D .

Scheme VIII. Proposed Epimerization Mechanism



III. PUBLICATIONS

DE-FG02-85ER13411, 7/1/89-present

A. In Print or In Press

1. "Optical Resolution and Absolute Configuration of the Chiral Pentamethylcyclopentadienyl Rhenium Carbonyl Complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CO})]^+ \text{BF}_4^-$ ", Y.-H. Huang, F. Niedercorn, A.M. Arif, and J.A. Gladysz, J. Organomet. Chem., **383**, 213-225 (1990).
2. "Synthesis and Properties of Chiral Rhenium Ether Complexes of the Formula $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{OR}_2)]^+ \text{X}^-$ ", S. Agbossou, J.M. Fernández, and J.A. Gladysz, Inorg. Chem. **29**, 476-480 (1990).
3. "Synthesis, Structure, and Reactivity of the Chiral Rhenium Phenyl Complex $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{C}_6\text{H}_5)$ ", S.K. Agbossou, G.S. Bodner, A.T. Patton, and J.A. Gladysz, Organometallics, **9**, 1184-1191 (1990).
4. "Isomerization of Diastereomeric Alkene Complexes of the Formula $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{H}_2\text{C}=\text{CHR})]^+$; the Alkene Enantioface Bound to the Metal can "Flip" Without Alkene Dissociation", T.-S. Peng and J.A. Gladysz, J. Chem. Soc., Chem. Commun., 902-903 (1990).
5. "Mechanism of Equilibration of Diastereomeric Rhenium Amide Complexes of the Formula $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{NHCHR}'')$; Rhenium vs. Carbon Epimerization", M.A. Dewey and J.A. Gladysz, Organometallics, **9**, 1351-1353 (1990).
6. "Synthesis and Reactivity of Chiral Rhenium Alcohol Complexes of the Formula $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{ROH})]^+ \text{BF}_4^-$ ", S.K. Agbossou, W.W. Smith, and J.A. Gladysz, Chemische Berichte, **123**, 1293-1299 (1990).
7. "A New Carbon-Hydrogen Bond Activation Reaction: Abstraction of Vinyl η Protons from Rhenium Alkene Complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{H}_2\text{C}=\text{CHR})]^+ \text{BF}_4^-$ by the Weak Base $t\text{-BuO}^- \text{K}^+$ ", T.-S. Peng and J.A. Gladysz, Organometallics **1990**, **9**, 2884-2886.
8. " π/σ Equilibria in Metal Complexes of Organic Carbonyl Compounds; Synthesis and Structure of Chiral Rhenium Aromatic Aldehyde Complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{O}=\text{CHAR})]^+ \text{X}^-$ ", N. Quirós Méndez, A.M. Arif, and J.A. Gladysz, Angew. Chem., Int. Ed. Engl. **1990**, **29**, 1473-1474.
9. "Synthesis, Structure, and Reactivity of Chiral Rhenium Alkyne Complexes of the Formula $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{RC}\equiv\text{CR}')]^+ \text{BF}_4^-$ ", J.J. Kowalczyk, A.M. Arif, and J.A. Gladysz, Organometallics **1991**, **10**, 1079-1088.
10. "Synthesis, Structure, and Reactivity of Chiral Rhenium Cycloalkene Complexes of the Formula $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}=\text{CH}(\text{CH}_2)_{n-2})]^+ \text{BF}_4^-$; Facile Vinyl η Deprotonation of a Coordinated Alkene", J.J. Kowalczyk, A.M. Arif, and J.A. Gladysz, Chemische Berichte **1991**, **124**, 729-742.
11. " π/σ Equilibria in Rhenium Ketone Complexes $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{O}=\text{CRR}')^+ \text{X}^-$; A Marked Electronic Effect Upon the Binding Mode", D.P. Klein, D.M. Dalton, N. Quirós Méndez, A.M. Arif, and J.A. Gladysz, J. Organomet. Chem., **412**, C7-C10 (1991).

12. "A New Catalyst for the Epimerization of Secondary Alcohols; Carbon-Hydrogen Bond Activation in the Rhenium Alkoxide Complexes $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{OCHRR}')$ ", I. Saura-Llamas, C.M. Garner, and J.A. Gladysz, Organometallics, **10**, 2533-2535 (1991).
13. "Mechanism of Isomerization of Alkylidene Complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(=\text{CHCHRR}')^+ \text{X}^-]$ to Alkene Complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{H}_2\text{C}=\text{CRR}')^+ \text{X}^-]$; Highly Stereoselective Wagner-Meerwein-type Rearrangements", C. Roger, G.S. Bodner, W.G. Hatton, and J.A. Gladysz, Organometallics, **10**, in press (1991).
14. "Reactions of the Terminal Rhenium Acetylide Complex $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{C}\equiv\text{CH})$ and $n\text{-BuLi}$; Generation, Alkylation, and Stannylation of Lithiocarbide Complexes of the Formula $(\eta^5\text{-C}_5\text{H}_4\text{X})\text{Re}(\text{NO})(\text{PPh}_3)(\text{C}\equiv\text{CLi})$ ", J.A. Ramsden, F. Agbossou, D.R. Senn, and J.A. Gladysz, J. Chem. Soc., Chem. Commun., in press (1991).

B. Submitted or in Preparation

15. "Cyclopentadienyl Rhenium Complexes", F. Niedercorn, E.J. O'Connor, C.M. Garner, N. Quirós Méndez, J.M. Fernández, A.T. Patton, and J.A. Gladysz, Inorganic Syntheses, in press.
16. "Epimerization of Secondary Alcohols by New Homogeneous, Low Oxidation-State Metal Catalysts; Carbon-Hydrogen Bond Activation in Rhenium Alkoxide Complexes $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{OCHRR}')$ ", I. Saura-Llamas and J.A. Gladysz, submitted to J. Am. Chem. Soc.
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