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## Ligand Intermediates in Metal-Catalyzed Reactions

Annual Technical Report

DE-FG03-93ER14321

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research period summarized in report: 8/1/92-8/1/93

August 10, 1993

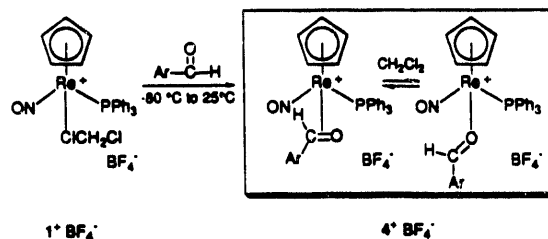
Four new papers have appeared in print since the beginning of the project period (#76-79) on January 1, 1993. Principal achievements are as follows.

A.  $\pi/\sigma$  Equilibria in Aldehyde and Ketone Complexes (pub. #76)

Aldehydes are reactants, intermediates, or products in many metal-catalyzed reactions. We have sought to identify the factors that influence the thermodynamics of  $\pi/\sigma$  binding, and delineate differences in reactivity between the two binding modes.

Thus, as was detailed in our 1992 renewal, fifteen aromatic aldehyde complexes of the formula  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{O}=\text{CHAr})]^+ \text{BF}_4^-$  ( $4^+ \text{BF}_4^-$ , Scheme I) have been prepared. IR analyses show  $4^+ \text{BF}_4^-$  to be >96:4 to 15:85 mixtures of  $\pi/\sigma$  isomers ( $\nu_{\text{NO}}$   $\pi/\sigma$  1745-1733/1701-1692  $\text{cm}^{-1}$ ). In general, electron withdrawing substituents (which enhance aldehyde  $\pi$  acidity and lower  $\sigma$  basicity) favor the  $\pi$  binding mode, whereas electron donating substituents have an opposite effect. Aliphatic aldehyde complexes of I exhibit only the  $\pi$  binding mode. This suggests that aryl/C=O conjugation stabilizes the  $\sigma$  isomer of benzaldehyde complex  $4i^+ \text{BF}_4^-$ .

**Scheme I. Synthesis of and IR Data for Aromatic Aldehyde Complexes  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{O}=\text{CHAr})]^+ \text{BF}_4^-$  ( $4^+ \text{BF}_4^-$ )**



Complex	IR $\nu_{\text{NO}}$ <sup>a</sup>		$\pi/\sigma$ <sup>b</sup>	$K_{\text{eq}}$ <sup>c</sup>	$\Delta G$ (cal/mol)
	$\pi$	$\sigma$			
Ar =					
a. $\text{C}_6\text{F}_5$	1748	b	>96:4	-	-
b. $4\text{-C}_6\text{H}_4\text{CF}_3$	1742	b	>96:4	-	-
c. $3\text{-C}_6\text{H}_4\text{CF}_3$	1741	b	>96:4	-	-
d. $3\text{-C}_6\text{H}_4\text{OCH}_3$	1738	1701	80:10	0.11	1301
e. $2\text{-C}_6\text{H}_4\text{OCH}_3$	1738	1700	89:11	0.12	1241
f. $4\text{-C}_6\text{H}_4\text{Cl}$	1740	1701	89:17	0.20	980
g. $4\text{-C}_6\text{H}_4\text{F}$	1738	1701	83:17	0.21	928
h. 1-naphthyl	1741	1700	82:18	0.23	881
i. $\text{C}_6\text{H}_5$	1738	1702	84:16	0.20	972
j. $3,4,5\text{-C}_6\text{H}_2(\text{OCH}_3)_3$	1738	1697	64:36	0.56	360
k. $4\text{-C}_6\text{H}_4\text{C}_6\text{H}_5$	1738	1700	64:36	0.57	334
l. $4\text{-C}_6\text{H}_4\text{CH}_3$	1738	1698	53:47	0.87	98
m. $2,4\text{-C}_6\text{H}_3(\text{OCH}_3)_2$	1738	1692	25:75	3.07	-488
n. $3,4\text{-C}_6\text{H}_3(\text{OCH}_3)_2$	1733	1694	24:76	3.18	-482
o. $4\text{-C}_6\text{H}_4\text{OCH}_3$	1733	1693	15:85	5.87	-1050

<sup>a</sup> In  $\text{CH}_2\text{Cl}_2$  at 28 °C. <sup>b</sup> No absorption observed; detection limit < 4%. <sup>c</sup> We assign error limits of  $\pm 2$  to each component of the normalized site ratios; e.g. 84:16 = (84  $\pm$  2):(16  $\pm$  2). <sup>d</sup> Due to rounded protocols, compounds with identical site ratios can give different  $K_{\text{eq}}$ .

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## **DISCLAIMER**

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Interestingly, the  $\pi/\sigma$  ratios increase in more polar solvents and at low temperatures. Apparently, the positive charge is more localized in the metal-lacyclopropane-like  $\pi$  isomers, providing stronger solvation. Van't Hoff plots ( $4i,1,o^+ BF_4^-$ ) give  $\Delta H$  of 3.6, 2.8, and 1.8 kcal/mol, and  $\Delta S$  of 9.2, 9.5, and 9.1 eu. The  $\sigma$  isomers also exhibit characteristic visible absorptions, assigned to metal-to-ligand charge transfer, as depicted in Figure 2. The crystal structure of  $\sigma-4o^+ BF_4^-$  shows a conjugated aryl/C=O/Re linkage, with a N-Re-O-C torsion angle of  $0^\circ$ . The CPMAS  $^{13}C$  NMR spectrum of  $4m^+ BF_4^-$  exhibits a HC=O resonance at 196.2 ppm (Figure 3), indicating that only the  $\sigma$  isomer is present in the solid state.

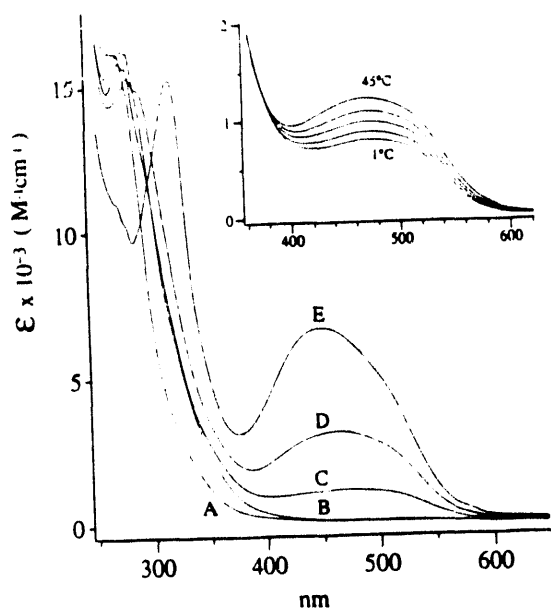


Figure 1. UV-visible spectra of aromatic aldehyde complexes ( $CH_2Cl_2$ , ambient temperature,  $1.0-2.0 \times 10^{-4}$  M): trace A, pentafluorobenzaldehyde complex  $4a^+ BF_4^-$ ; trace B, *p*-trifluoromethylbenzaldehyde complex  $4b^+ BF_4^-$ ; trace C, benzaldehyde complex  $4i^+ BF_4^-$ ; trace D, *p*-methylbenzaldehyde complex  $4l^+ BF_4^-$ ; trace E, *p*-methoxybenzaldehyde complex  $4o^+ BF_4^-$ ; inset,  $4i^+ BF_4^-$  at 45 (top), 30, 20, 10, and 1  $^\circ C$ .

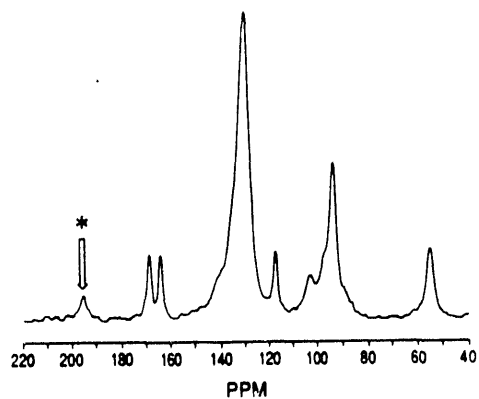
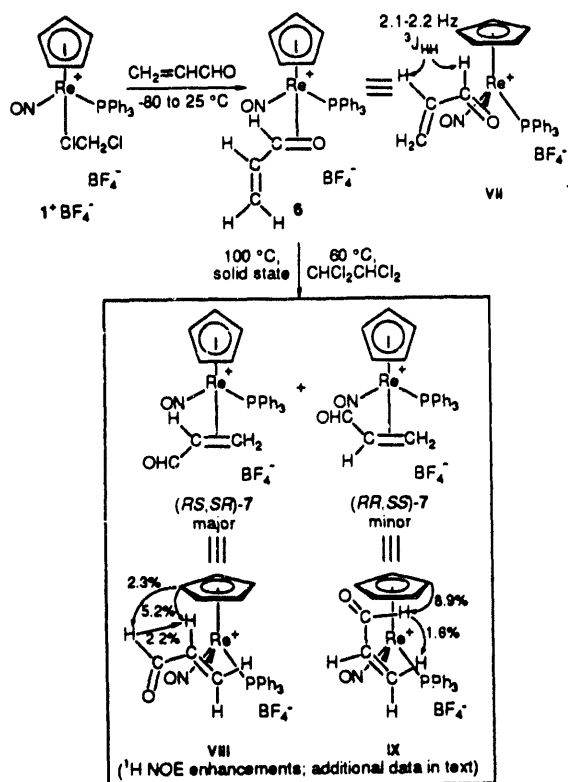


Figure 2. CPMAS  $^{13}C$  NMR spectrum of a  $CH_2Cl_2$  hemisolvate of 2,4-dimethoxybenzaldehyde complex  $[(\eta^5-C_5H_5)Re(NO)(PPh_3)(O=CH-2,4-C_6H_3(OCH_3)_2)]^+ BF_4^- (4m^+ BF_4^- \cdot (CH_2Cl_2)_{0.5})$ . The \* indicates the HC=O resonance (196.2 ppm).

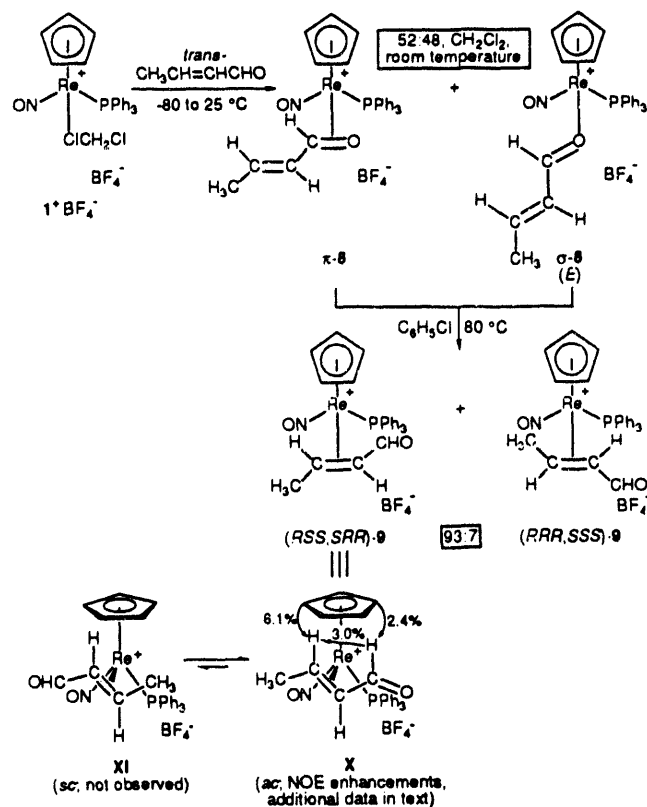
### B. Thermodynamic Ligand Binding Affinities; $\alpha,\beta$ Unsaturated Organic Carbonyl Compounds (pub #77)

We have discovered that  $\alpha,\beta$ -unsaturated carbonyl compounds exhibit completely divergent kinetic and thermodynamic binding affinities for the prototype 16-valence-electron metal fragment  $[(\eta^5-C_5H_5)Re(NO)(PPh_3)]^+$ . We have studied this behavior in detail for a variety of compounds, and the principal conclusions can be obtained visually from Schemes II-VII. Hence, a single metal center can be used to activate either (or both) of two functional groups, depending upon conditions.

Scheme II. Binding of Acrolein to the Chiral Lewis Acid  
 Acid  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)]^+ \text{BF}_4^-$  (I)

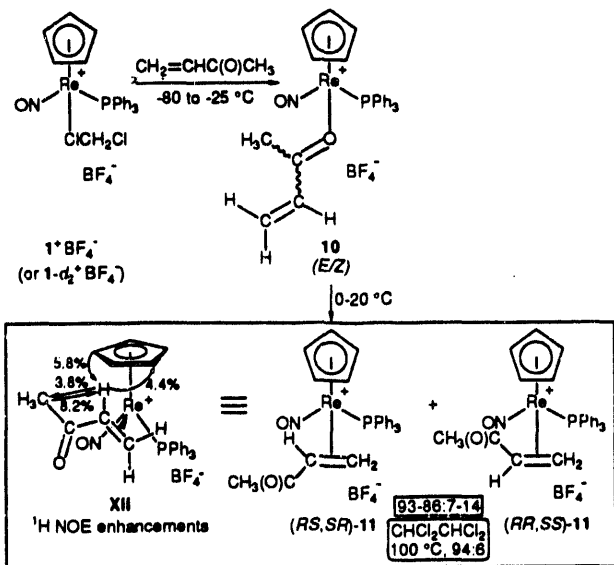


Scheme III. Binding of Crotonaldehyde to the Chiral Lewis Acid I

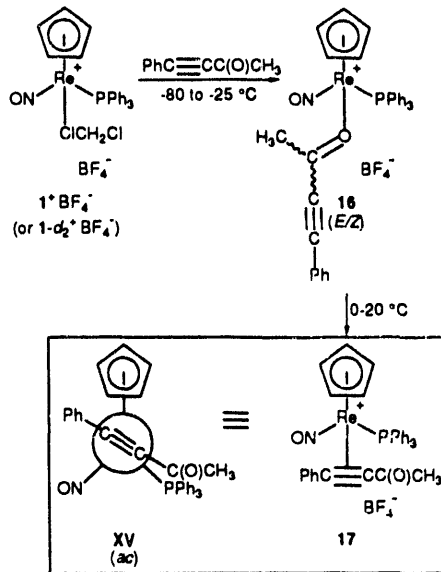


Thus, acrolein first gives a  $\pi$  O=C complex, which cleanly isomerizes in the solid state (100 °C) to a  $\pi$  C=C complex (Scheme II). Crotonaldehyde gives both  $\pi$  and  $\sigma$  O=C complexes (52:48,  $\text{CH}_2\text{Cl}_2$ , room temperature), which convert at 80 °C to a  $\pi$  C=C complex (Scheme III). Methyl vinyl ketone gives a  $\sigma$  O=C complex, which is characterized by NMR at -25 °C. At room temperature, a  $\pi$  C=C complex forms (Scheme IV). Cyclopentenone and cyclohexenone give  $\sigma$  O=C complex forms (Scheme IV). Cyclopentenone and cyclohexenone give  $\sigma$  O=C complexes that only partially isomerize to  $\pi$  C=C complexes at 60-90 °C (Scheme V). The acetylenic ketone 4-phenyl-3-butyne-2-one gives a  $\sigma$  O=C complex at -25 °C. At room temperature, a  $\pi$  C $\equiv$ C complex forms (Scheme VI). Other acyclic vinyl ketones follow the preceding reactivity patterns (Scheme VII). The crystal structure of a  $\pi$  C=C complex of trans-4-hexen-3-one has been determined. The NMR, configurational, and conformational properties of the preceding complexes, all of which can exist in several isomeric forms, have been analyzed in detail.

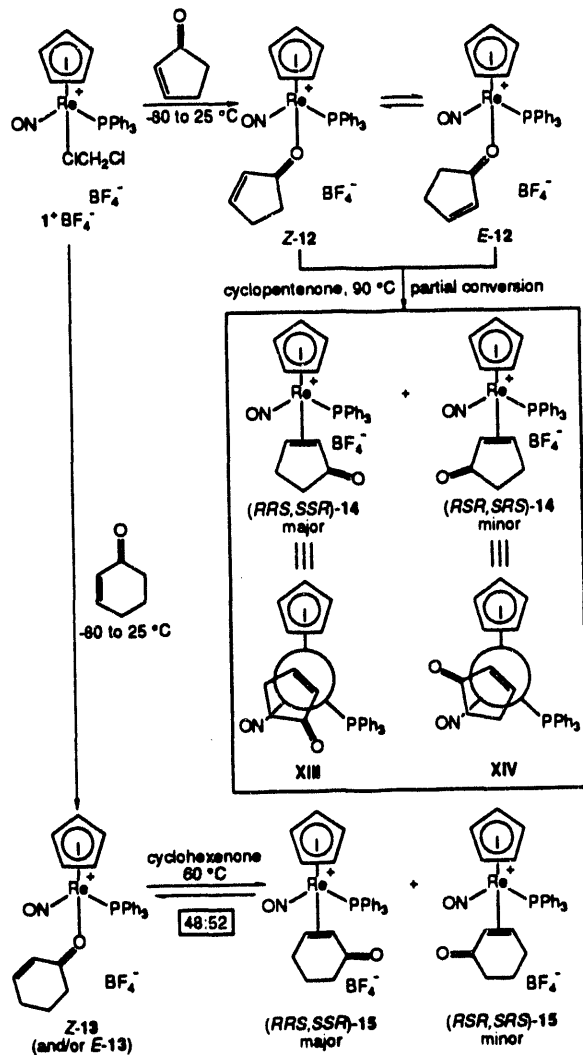
Scheme IV. Binding of Methyl Vinyl Ketone to the Chiral Lewis Acid I



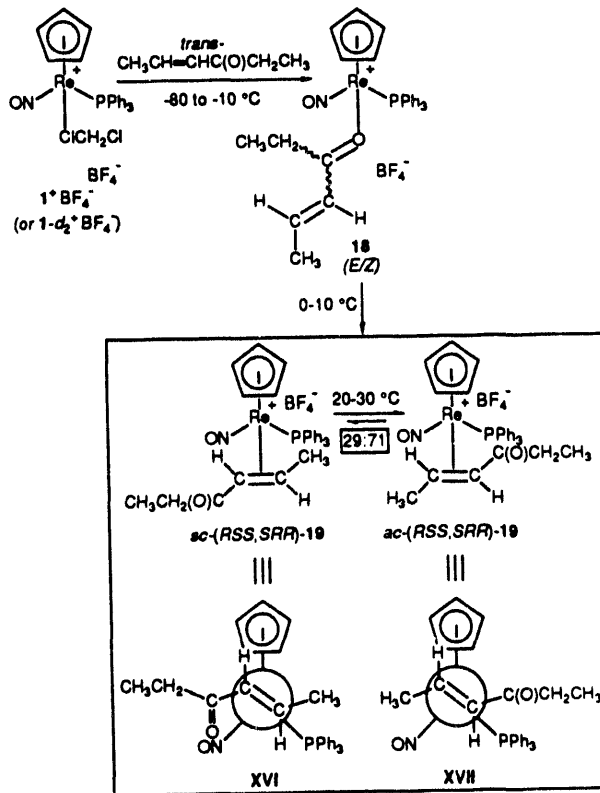
Scheme VI. Binding of an Acetylenic Ketone to the Chiral Lewis Acid I



Scheme V. Binding of Cycloalkenones to the Chiral Lewis Acid I



Scheme VII. Binding of *trans*-4-Hexen-3-one to the Chiral Lewis Acid I

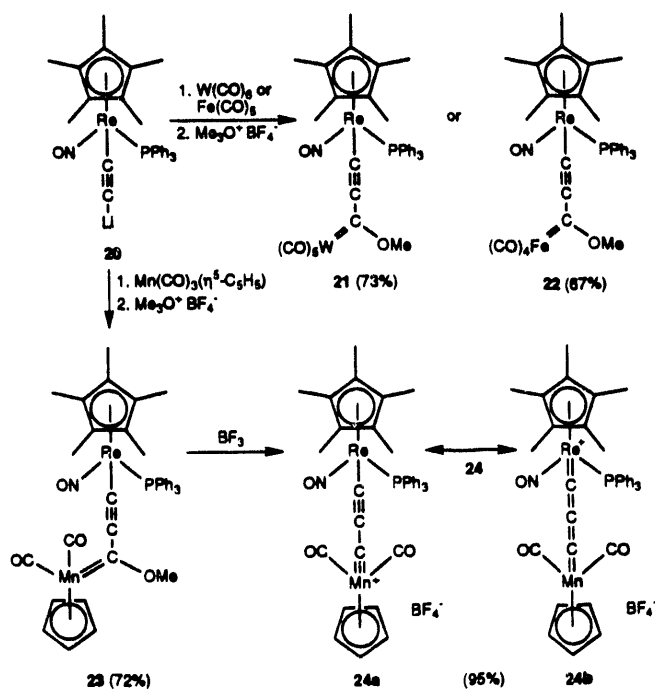


C. A New Form of Coordinated Carbon: an Unsupported C<sub>3</sub> Chain that Spans Two Different Transition Metals (pub #78)

Transition metal complexes of carbon, C<sub>x</sub>, are of interest both as models for carbide species that are generated on heterogeneous catalysts used in processing basic chemical feedstocks, and in the context of the many new carbon allotropes that have recently become available. Last year, we reported convenient new methodology for C<sub>2</sub> complexes that involved the deprotonation of ethynyl complexes L<sub>n</sub>MC≡CH to the corresponding conjugate bases L<sub>n</sub>MC≡C<sup>-</sup>. The latter readily react with a variety of electrophiles.

We have now found that the lithiated rhenium ethynyl complex species (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Re(NO)(PPh<sub>3</sub>)(C≡CLi) attacks the carbon monoxide ligands in W(CO)<sub>6</sub>, Fe(CO)<sub>5</sub> and Mn(CO)<sub>3</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>). Addition of Me<sub>3</sub>O<sup>+</sup>BF<sub>4</sub><sup>-</sup> gives the bimetallic Fischer carbene or C<sub>3</sub>OMe complexes (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Re(NO)(PPh<sub>3</sub>)(C≡C-C(OMe)=)M(CO)<sub>x</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>y</sub> (M/x/y = 21, W/5/0; 22, Fe/4/0; 23, Mn/2/1), as shown in Scheme VIII. The crystal structure of 21, which is shown in Figure 3, and spectroscopic properties indicate contributions by <sup>+</sup>Re=C=C=C(OMe)-M<sup>-</sup> resonance forms. Reaction of 23 and BF<sub>3</sub> (Scheme VIII) gives [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Re(NO)(PPh<sub>3</sub>)(CCC)Mn(CO)<sub>2</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)]<sup>+</sup>BF<sub>4</sub><sup>-</sup> (24) -- the first compound with an unsupported C<sub>3</sub> chain spanning two transition metals. Spectroscopic and crystallographic properties establish a dominant structural contribution by a fully cumulated <sup>+</sup>Re=C=C=C=Mn resonance

Scheme VIII. Synthesis of C<sub>3</sub>-OMe and C<sub>3</sub> Complexes





form. Complexes 21-24 also exhibit distinctive UV/visible absorptions, as shown in Figure 4. Those of 24 likely arise from metal-to-metal charge transfer. Investigation of the chemical properties of 24 is in progress.

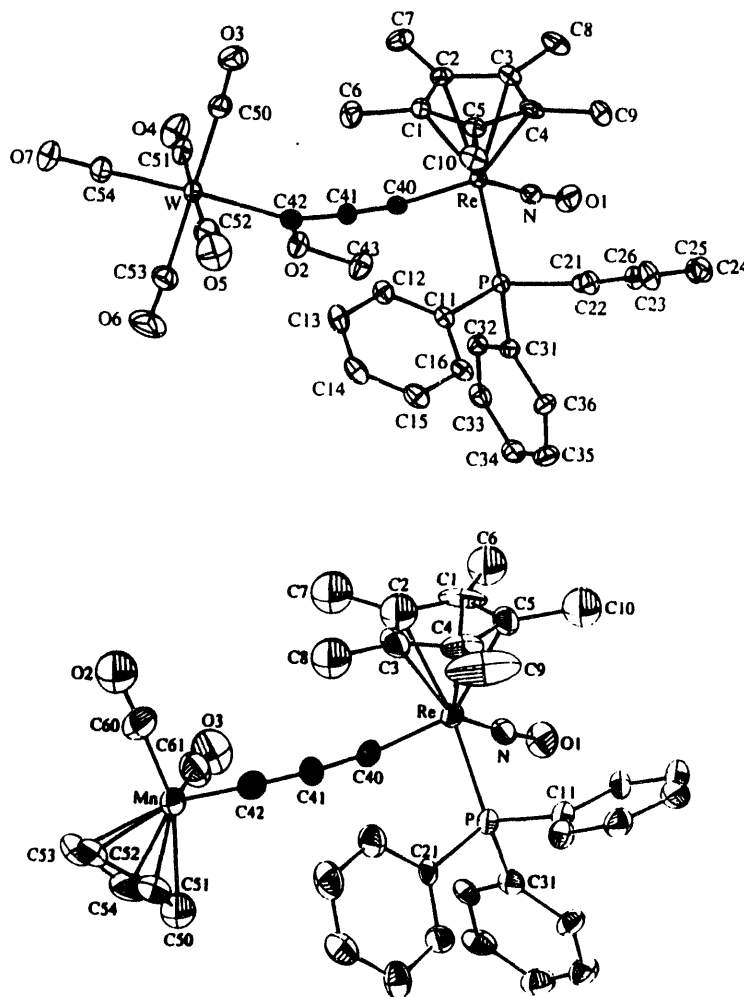


Figure 3. Structures of  $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{C}\equiv\text{C}-\text{C}(\text{OMe})=\text{W}(\text{CO})_5)$  (21, top) and the cation of a hemisolvate of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CCC})\text{Mn}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]^+\text{BF}_4^-$  ( $24 \cdot (\text{CH}_2\text{Cl}_2)_{0.5}$ , bottom). Selected bond lengths (Å) and angles ( $^\circ$ ): 21, Re-C40 1.973(7), C40-C41 1.23(1), C41-C42 1.38(1), C42-O2 1.353(9), C42-W 2.200(8), Re-P 2.398(2), Re-N 1.763(6), Re-C40-C41 172.3(7), C40-C41-C42 174.5(8), C41-C42-O2 116.5(7), C41-C42-W 128.1(6);  $24 \cdot (\text{CH}_2\text{Cl}_2)_{0.5}$  (two independent cations), Re-C40 1.92(1)/1.93(1), C40-C41 1.26(2)/1.28(2), C41-C42 1.32(2)/1.28(2), C42-Mn 1.75(2)/1.75(2), Re-P 2.413(4)/2.410(4), Re-N 1.76(1)/1.75(1), Re-C40-C41 173(1)/175(1), C40-C41-C42 175(2)/170(2), C41-C42-Mn 178(1)/178(2).

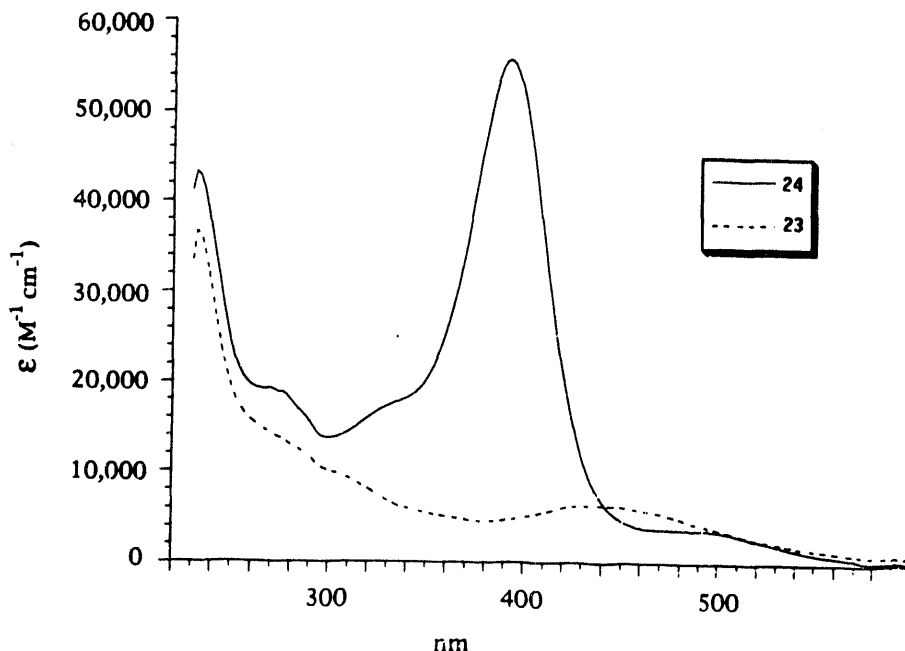


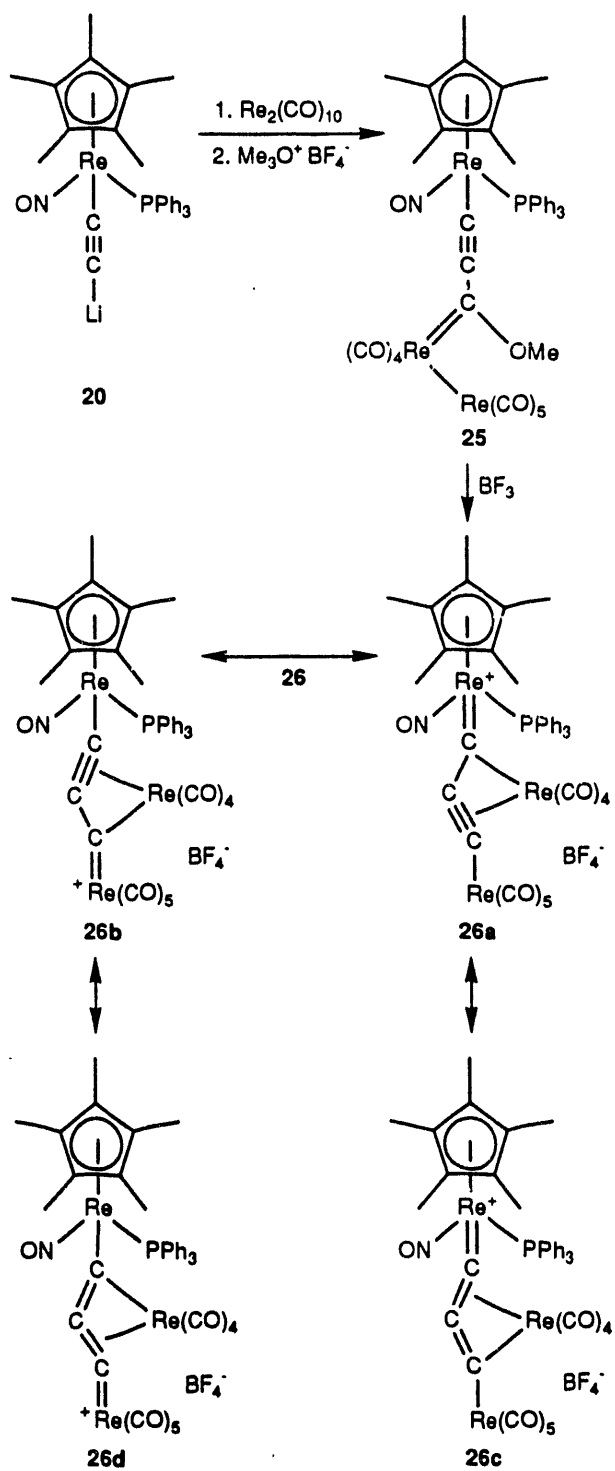
Figure 4. UV/visible spectra of 23 and 24 ( $\text{CH}_2\text{Cl}_2$ , ambient temperature,  $3.0\text{--}3.9 \times 10^{-5}$  M).

D. A New Form of Coordinated Carbon: an  $\text{C}_3$  Chain that is Anchored by a Metal on Each End and Spanned by a Third (pub #79)

We sought to study the effect of replacing the monometallic carbonyl compounds utilized in Scheme VIII with polymetallic carbonyl compounds. We thought there would be a good chance that one of the  $\text{C}_3$  ligand termini would bridge to a second metal (although the exact identity of the final product would be difficult to predict).

Thus, reaction of  $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{C}\equiv\text{CLi})$  with  $\text{Re}_2(\text{CO})_{10}$  and then  $\text{Me}_3\text{O}^+ \text{BF}_4^-$  gives the trirhenium alkynyl Fischer carbene complex cis- $(\eta^5\text{-C}_5\text{Me}_5)\text{-Re}(\text{NO})(\text{PPh}_3)(\text{C}\equiv\text{C}(\text{OMe})=\text{Re}(\text{CO})_4)\text{Re}(\text{CO})_5$  (25) in 92% yield, as shown in Scheme IX. NMR and IR properties indicate a substantial contribution by a  $^+\text{Re}=\text{C}=\text{C}=\text{C}(\text{OMe})\text{-Re}^-$  resonance form. Reaction of 25 and  $\text{BF}_3$  gives the extremely unusual  $\text{C}_3$  complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\mu\text{-}\eta^1\text{:}\eta^3\text{:}\eta^1\text{-CCC})(\text{Re}(\text{CO})_4)\text{Re}(\text{CO})_5]^+ \text{BF}_4^-$  (26) in 64% yield (Scheme IX). Complex 26 is likely derived by initial methoxide abstraction from 25, followed by rhenium-rhenium bond cleavage. The crystal structure, which is depicted in Figure 5, shows a slightly bent  $\text{C}_3$  linkage ( $152(4)^\circ$ ) that is bound by a rhenium on each end, and spanned by a  $\text{Re}(\text{CO})_4$  moiety. NMR, IR, and crystallographic properties suggest that 26 is best viewed as a completely metalated  $\pi$  propargyl complex of  $\text{Re}(\text{CO})_4$ .

Scheme IX. Synthesis of  $\text{Re}_3\text{C}_3$  Complexes



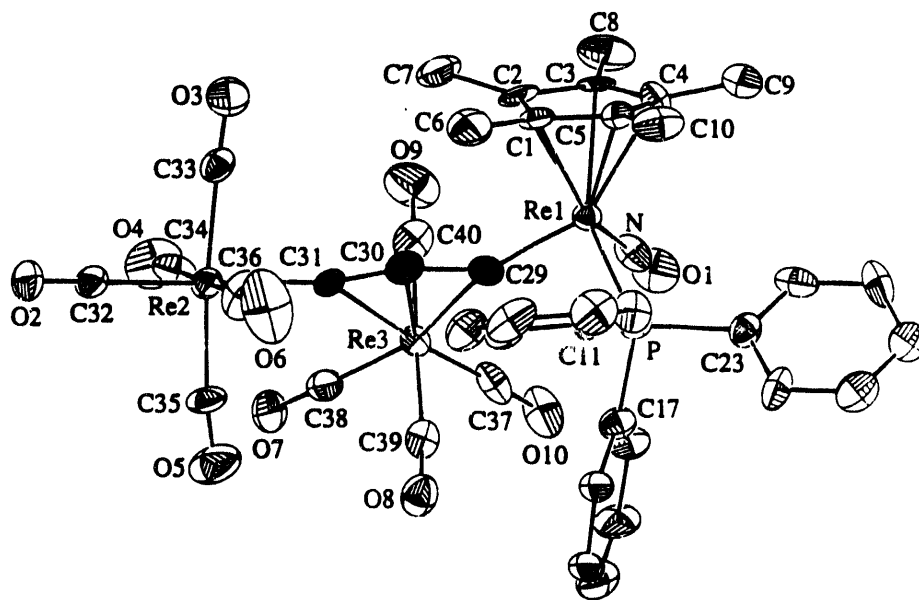


Figure 5. Structure of the cation of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\mu\text{-}\eta^1:\eta^3:\eta^1\text{-CCC})\text{-}(\text{Re}(\text{CO})_4)\text{Re}(\text{CO})_5]^+\text{BF}_4^-$  (26). Selected bond lengths (Å) and angles ( $^\circ$ ): Re1-C29 1.94(3), C29-C30 1.41(6), C30-C31 1.28(5), C31-Re2 2.09(4), Re3-C29 2.24(3), Re3-C30 2.27(4), Re3-C31 2.43(4), Re1-P 2.440(9), Re1-N 1.73(3), Re1-C29-C30 140(3), C29-C30-C31 152(4), C30-C31-Re2 155(3).

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PUBLICATIONS

DE-FG03-93ER14321, 1/1/93-12/31/93

76. "Synthesis, Structure, and Spectroscopic Properties of Chiral Rhenium Aromatic Aldehyde complexes  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{O}=\text{CHR})]^+ \text{X}^-$ ; Equilibria between  $\pi$  and  $\sigma$  Aldehyde Binding Modes", N. Quirós Méndez, J.W. Seyler, A.M. Arif, and J.A. Gladysz, J. Am. Chem. Soc. 115, 2323-2334 (1993).
77. "A New Form of Coordinated Carbon: An Unsupported  $\text{C}_3$  Chain Spanning Two Different Transition Metals", W. Weng, J.A. Ramsden, A.M. Arif, J.A. Gladysz, J. Am. Chem. Soc., 115, 3824-3825 (1993).
78. (a) "A New Form of Coordinated Carbon: A  $\text{C}_3$  Chain that is Anchored by a Transition Metal on Each End and Spanned by a Third", W. Weng, A.M. Arif, and J. A. Gladysz, Angew. Chem., Int. Ed. Engl., 32, 891-892 (1993).  
(b) "Ein neuer Kohlenstoffligand; eine durch ein Re-Atom überdachte Re- $\text{C}_3$ -Re-Kette" W. Weng, A.M. Arif, and J.A. Gladysz, Angewandte Chemie, 105, 937-938 (1993).
79. Synthesis and Structure of Complexes of  $\alpha,\beta$ -Unsaturated Carbonyl Compounds and the Chiral Rhenium Fragment  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)]^+$ ; Divergent Kinetic and Thermodynamic  $\text{C}=\text{O}/\text{C}=\text{C}$  and  $\text{C}=\text{O}/\text{C}\equiv\text{C}$  Binding Selectivities", Y. Wang, F. Agbossou, D.M. Dalton, Y. Liu, A.M. Arif, and J.A. Gladysz, Organometallics, 12, 2699-2713 (1993).
80. "A New, Stereospecific Alkene Metalation Reaction; Facile Vinylic Carbon-Hydrogen Bond Activation in Chiral Rhenium Complexes  $[(\eta^5\text{-C}_5\text{R}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{H}_2\text{C}=\text{CHR})]^+ \text{BF}_4^-$ ", T.-S. Peng and J.A. Gladysz, in preparation for J. Am. Chem. Soc.

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Theses

1. Edward J. Fairfax, 1/92-3/93, "Complexes of the Chiral Rhenium Fragment  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)]^+$  and Non-Conjugated Keto-Alkenes; Divergent Kinetic and Thermodynamic  $\text{C}=\text{O}/\text{C}=\text{C}$  Binding Properties", MS Dissertation, University of Utah, 1993.

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EXPENDITURES, CURRENT FISCAL YEAR

(1) All of the \$120,000 budgeted for the current DE-FG01-85ER13411 grant period (1/1/93-12/31/93) will be expended by 12/31/93. As of 8/1/93, over \$90,000 has been expended or committed.

OTHER RESEARCH SUPPORT

A. Current Federal Support

1. National Institutes of Health (GM 31280-10)  
"Asymmetric Synthesis Using Chiral Organorhenium Complexes"  
March 1, 1992 to February 29, 1996  
\$522,583 (four years, direct costs)  
Principal Investigator effort: 0.5-1.0 month summer (research conducted at the University of Utah)
2. National Science Foundation (CHE-9107489)  
"Chemistry of Transition Metal/Main Group Element Compounds"  
July 1, 1991 to June 30, 1994  
\$210,620 (three years, direct costs)  
Principal Investigator effort: 0.5-1.0 month summer (research conducted at the University of Utah)
3. Department of Energy (this grant)  
"Ligand Intermediates in Metal Catalyzed Reactions"  
January 1, 1993 to December 31, 1995  
\$254,728 (3 years, direct costs)  
Principal Investigator effort: 0.5-1.0 month summer (research conducted at the University of Utah)

B. Pending

none; no other Federal grants are planned for submission through 1993.

**DATE**

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**END**

