Ligand Intermediates in Metal-Catalyzed Reactions

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Exciting breakthroughs were made on a variety of projects, as summarized below.

A. Linkage Isomerism in Imine Ligands that are Catalytic Intermediates (paper 85).

Reaction of the amido complex $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{NH}_2)$ (**2**) and hexafluoroacetone gives the methyleneamido complex $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{N}=\text{C}(\text{CF}_3)_2)$ (**3**, 58%). Addition of TfOH to **3** yields the σ imine complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\eta^1\text{-N(H)=C}(\text{CF}_3)_2)]^+\text{TfO}^-$ (**4**, 96%). Similar reactions of **2** with trifluoroacetaldehyde and then TfOH give the σ imine complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\eta^1\text{-N(H)=C}(\text{CF}_3)\text{H})]^+\text{TfO}^-$ (**5**, 78%), and sometimes small amounts of the corresponding π trifluoroacetaldehyde complex. Reaction of **5** and $t\text{-BuO}^- \text{K}^+$ gives the methyleneamido complex $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{N}=\text{C}(\text{CF}_3)\text{H})$ (**6**, 82%). The IR and NMR properties of **3-6** are studied in detail. The ^{13}C NMR spectra show C=N signals (157-142 ppm) diagnostic of σ binding modes. No evidence is observed for π isomers of **4** or **5**. Analogous $\text{O}=\text{C}(\text{CF}_3)\text{X}$ complexes give exclusively π isomers, and rationales are discussed. Reactions of **3** or **6** with MeOTf and heteroatom electrophiles are also described.

B. Phosphine Ligand Lability in Amido Complexes (paper 86).

The diastereomerically and enantiomerically pure amido complex $(SR)\text{-}(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{NHCH}(\text{CH}_3)\text{Ph})$ ($(SR)\text{-5}$) converts to $(RR)\text{-5}$ (inversion at rhenium, retention at carbon) in THF- d_8 at 49.4 °C with $k_1 = 2.34 \times 10^{-4} \text{ s}^{-1}$ and $k_{-1} = 0.90 \times 10^{-4} \text{ s}^{-1}$. Similarly, $(SS)\text{-5}$ converts to $(RS)\text{-5}$ with $k_1 = 0.90 \times 10^{-4} \text{ s}^{-1}$ and $k_{-1} = 2.30 \times 10^{-4} \text{ s}^{-1}$. Both epimerizations give equilibrium ratios (RR/SR or SS/RS) of 70:30. Reactions with HOTf yield $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{NH}_2\text{CH}(\text{CH}_3)\text{Ph})]^+\text{TfO}^-$, and subsequent additions of $\text{Et}_4\text{N}^+ \text{CN}^-$ afford $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CN})$ and $\text{NH}_2\text{CH}(\text{CH}_3)\text{Ph}$ (all steps with retention at rhenium and carbon). Enantiomeric purities and absolute configurations are assayed by chiral NMR shift reagents and (-)-menthyl chloroformate derivatives, respectively, establishing configurations of epimerized **5**. Reaction of $(SR)\text{-5}$ and $\text{P}(p\text{-tol})_3$ in THF- d_8 at 49.4 °C gives $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{P}(p\text{-tol})_3)(\text{NHCH}(\text{CH}_3)\text{Ph})$ (50:50 (t_0) $\rightarrow$ 66:34 (t_∞) RR/SR) with $k = 4.6 \times 10^{-4} \text{ s}^{-1}$, twice that for the conversion of $(SR)\text{-5}$ to $(RR)\text{-5}$. Rate data for the latter at 32.3-59.1 °C give $\Delta H^\ddagger = 26 \text{ kcal/mol}$ and $\Delta S^\ddagger = 6 \text{ eu}$. These results are best modeled by mechanisms involving initial and rate determining PPh_3 dissociation, with anchimeric assistance by the amido lone pair, to give an intermediate that is trigonal planar at rhenium and combines with PAr_3 without significant diastereoselectivity. Reactions of $n\text{-BuLi}$ with **5** and related complexes give LiR species from which PPh_3 is lost at lower temperatures, and are presumed to be much less configurationally stable.

C. Synthesis, Structure and Reactivity of Trimetallic Rhenium/Rhenium and Tetrametallic Rhenium/Osmium Carbide Complexes (paper 88).

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 C_3OMe complex $cis\text{-}(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{C}\equiv\text{CC}(\text{OMe})=)\text{-Re}(\text{CO})_4\text{Re}(\text{CO})_5$ (**3**, 92%). An analogous reaction with $\text{Os}_3(\text{CO})_{12}$ gives heterotetrametallic $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{C}\equiv\text{CC}(\text{OMe})=)\text{Os}_3(\text{CO})_{11}$ (**4**, 87%). NMR, IR, and crystallographic data (**4**) show substantial contributions by $^1\text{Re}=\text{C}=\text{C}(\text{OMe})\text{-M}^+$ resonance forms. Reaction of **3** and excess BF_3 gas in toluene precipitates $[(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\mu\text{-}\eta^1\text{:}\eta^3\text{:}\eta^1\text{-CCC})(\text{Re}(\text{CO})_4)\text{Re}(\text{CO})_5)]^+\text{BF}_4^-$ (**5**, 64%). A crystal structure shows a slightly bent C_3 moiety ($152(4)^\circ$) that binds a rhenium on each end and spans a third. NMR, IR, and bond length data show that **5** is best viewed as a completely metalated π propargyl or $\text{PRe}=\text{CC}\equiv\text{C-Re}(\text{CO})_5$ adduct of $\text{Re}(\text{CO})_4$. It is likely derived by initial methoxide abstraction

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from **3** to give a ReCCRe species, followed by rearrangement. Reaction of $(\eta^5\text{-C}_5\text{Me}_5)\text{-Re(NO)(PPh}_3\text{)(C}\equiv\text{CCl)}$ with $\text{Re}_2(\text{CO})_{10}$ and then $\text{Me}_3\text{O}^+\text{BF}_4^-$ gives the C_5OMe complex $\text{cis-}(\eta^5\text{-C}_5\text{Me}_5)\text{Re(NO)(PPh}_3\text{)(C}\equiv\text{CC(OMe)=Re(CO)}_4\text{Re(CO)}_5)$ (**8**, 44%). When **4** or **8** are treated with BF_3 gas, C_x complexes are not detected.

D. Synthesis, Structure and Reactivity of Tetrametallic Rhenium/Osmium Carbide Complexes (papers 87 and 93).

Reaction of $(\eta^5\text{-C}_5\text{Me}_5)\text{Re(NO)(PPh}_3\text{)(C}\equiv\text{CH)}$ and $\text{Os}_3(\text{CO})_{10}(\text{NCCH}_3)_2$ (CH_2Cl_2 , RT) gives the ReC_2Os_3 complex $(\eta^5\text{-C}_5\text{Me}_5)\text{Re(NO)(PPh}_3\text{)(CCOs}_3(\text{CO})_{10}(\text{H}))$ (**2**, 78%). A crystal structure shows that the hydride and ReCC terminus symmetrically bridge the same two osmium atoms. The ReC and ReCC bond lengths, and IR and NMR properties, indicate contributions by both $\text{Re-C}\equiv\text{C(Os}_3\text{)}$ and $^+\text{Re}=\text{C}=\text{C(Os}_3\text{)}^-$ resonance forms. Analogous ReC_4Os_3 (**4**, 83%) and ReC_6Os_3 (**6**, 61%) complexes are similarly prepared, and are progressively less stable in solution and the solid state. Cyclic voltammograms of **2**, **4**, and **6** show partially reversible oxidations. Complex **4** decarbonylates in refluxing hexane to give $(\eta^5\text{-C}_5\text{Me}_5)\text{-Re(NO)(PPh}_3\text{)(CCCCOs}_3(\text{CO})_9(\text{H}))$ (57%), in which the ReCCCC terminus bonds to three osmium atoms and the adjacent carbon (and hydride) to two. Reaction of **2** and $\text{HBF}_4\cdot\text{Et}_2\text{O}$ gives $[(\eta^5\text{-C}_5\text{Me}_5)\text{Re(NO)(PPh}_3\text{)(CCOs}_3(\text{CO})_{10}(\text{H})_2)]^+\text{BF}_4^-$ (69%). A crystal structure of the SbF_6^- salt shows a ReC_2Os_3 unit very similar to that of **2**, with the hydrides bridging different osmium-osmium bonds. The C_3OMe complex $(\eta^5\text{-C}_5\text{Me}_5)\text{Re(NO)(PPh}_3\text{)(C}\equiv\text{CC(OMe)=Os}_3(\text{CO})_{11})$ decarbonylates in refluxing heptane to give $(\eta^5\text{-C}_5\text{Me}_5)\text{Re(NO)(PPh}_3\text{)(CCC(Os}_3(\text{CO})_9(\text{OMe}))$ (63%), in which the ReCCC terminus bonds to three osmium atoms, and the center carbon bonds to the osmium that is not methoxide-bridged. A crystal structure shows the ReCCC carbon to be highly distorted, bonding to four atoms that fall on one side of a plane through the carbon.

E. Synthesis, Structure, and Reactivity of Heterobimetallic Complexes with C_3 and C_5 Carbide Bridges (paper 94).

Reactions of $(\eta^5\text{-C}_5\text{Me}_5)\text{Re(NO)(PPh}_3\text{)(C}\equiv\text{CLi)}$ with W(CO)_6 , Fe(CO)_5 or $\text{Mn(CO)}_5(\eta^5\text{-C}_5\text{H}_n\text{Cl}_{5-n})$, followed by $\text{Me}_3\text{O}^+\text{BF}_4^-$, give the heterobimetallic C_3OMe complexes $(\eta^5\text{-C}_5\text{Me}_5)\text{Re(NO)(PPh}_3\text{)(C}\equiv\text{CC(OMe)=M(CO)}_x(\eta^5\text{-C}_5\text{H}_n\text{Cl}_{5-n}))$, ($\text{M/x/y/n} = 3, \text{W/5/0/-}$; **4**, Fe/4/0/- ; **5**, Mn/2/1/5 ; **6**, Mn/2/1/4 ; **7**, Mn/2/1/0). Spectroscopic and crystallographic (**3**) data indicate contributions by $^+\text{Re}=\text{C}=\text{C(OMe)-M}^-$ resonance forms. Reactions of **4-7** and BF_3 gas give the title compounds $[(\eta^5\text{-C}_5\text{Me}_5)\text{Re(NO)(PPh}_3\text{)(CCC)M(CO)}_x(\eta^5\text{-C}_5\text{H}_n\text{Cl}_{5-n}))]$, ($\text{M/x/y/n} = 9, \text{Mn/2/1/5}$; **10**, Mn/2/1/4 ; **11**, Mn/2/1/0 ; **12**, Fe/4/0/-). Spectroscopic and crystallographic (**9**) data indicate dominant contributions by fully cumulated $^+\text{Re}=\text{C}=\text{C}=\text{C-Mn}$ resonance forms. Reactions of $(\eta^5\text{-C}_5\text{Me}_5)\text{Re(NO)(PPh}_3\text{)(C}\equiv\text{CC}\equiv\text{CLi)}$ with $\text{Mn(CO)}_3(\eta^5\text{-C}_5\text{Cl}_5)$, $\text{Mn(CO)}_3(\eta^5\text{-C}_5\text{Br}_5)$, or Fe(CO)_5 , followed by $\text{Me}_3\text{O}^+\text{BF}_4^-$, give the C_5OMe complexes $(\eta^5\text{-C}_5\text{Me}_5)\text{Re(NO)(PPh}_3\text{)(C}\equiv\text{CC}\equiv\text{CC(OMe)=M(CO)}_x(\eta^5\text{-C}_5\text{X}_5))$, ($\text{M/x/y/X} = 16, \text{Mn/2/1/Cl}$; **19**, Mn/2/1/Br ; **20**, Fe/4/0/-). However, $\text{Mn(CO)}_3(\eta^5\text{-C}_5\text{H}_5)$ does not react. Reaction of **16** and BF_3 gives the C_5 complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Re(NO)(PPh}_3\text{)(CCCCC)Mn(CO)}_2(\eta^5\text{-C}_5\text{Cl}_5)]^+\text{BF}_4^-$ (**21**) as a light-sensitive deep brown powder of >94% purity. IR and NMR data show a dominant $^+\text{Re}=\text{C}=\text{C}=\text{C}=\text{C-Mn}$ resonance form. UV-visible spectra of **9-11** and **21** show intense absorptions at 392, 396, 414, and 480 nm (ϵ 55800, 50900, 49100, 60500 $\text{M}^{-1}\text{cm}^{-1}$), respectively, and weaker longer wavelength bands. These are believed to have appreciable rhenium-to-manganese charge transfer character.

F. Synthesis, Structure, and Reactivity of Dirhenium Complexes with CN bridges (paper 90).

Reactions of $(\eta^5\text{-C}_5\text{R}'_5)\text{Re(NO)(PPh}_3\text{)(OTf)}$ (**1a/b**, $\text{R}' = \text{H/Me}$) and $(\eta^5\text{-C}_5\text{R}_5)\text{Re(NO)(PPh}_3\text{)(CN)}$ (**2a/b**, $\text{R} = \text{H/Me}$) in toluene or CH_2Cl_2 give the title complexes ($\text{R/R}' = \text{H/H}$ (**4a**), Me/H (**4b**), H/Me (**4c**), Me/Me (**4d**)) in 71-91% yields as >99:<1, 99-88:1-12, 95-66:5-34, and 71-60:29-40 mixtures of *SR,RS,SS,RR* diastereomers (pseudo *meso/dl*). Reaction of (*S*)-**1a** and (*R*)-**2a** gives (*RR*)-**4a** (retention) – a diastereomer not formed from the racemates. IR and NMR spectra of **4a-d** are analyzed, especially with reference to the cyanide ligands and charge distribution. Cyclic voltammetry shows pseudoreversible oxidations that become thermodynamically more favorable with increased numbers of pentamethylcyclopentadienyl ligands. A

crystal structure of (SR,RS)-4a shows a slightly bent ReCNRe linkage, bond lengths close to those of related ReC≡ and RC≡NRe compounds, and van der Waals contacts across the bridge. The diastereomers of 4a-d, and linkage isomers 4b,c, do not equilibrate in CDCl₃ (55 °C) or CHCl₂CHCl₂ (98 °C). The dissociation of 4a,d to 1a/2a or 1b/2b is excluded by unsuccessful trapping experiments involving 1a,b, 2a,b and diallyl sulfide (25-120 °C). However, the diallyl sulfide complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{S}(\text{CH}_2\text{CH}=\text{CH}_2)_2)]^+ \text{TfO}^-$ and 2a react (CHCl₂CHCl₂, 96 °C) to give 4a (75-63%: 50:50 SR,RS/SS,RR). These data show the cyanide bridges to have exceptional kinetic and thermodynamic stabilities.

G. Complexes and Catalysts Immobilized in Fluorinated Solvents: Mechanistic Studies (papers 89 and 92).

The reaction of $[\text{Ir}(\text{Cl})(\text{cod})]_2$, $\text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3)_3$, and CO (1 atm) gives the title compound (2, 97%). Tri(*n*-octyl) phosphine (3) and rhodium (4) analogs are similarly prepared. Crystal structures of 2 and 4 show anti CCCC conformations in the six perfluoroalkyl groups (average torsion angle 169°), with four chains (two per phosphorus) in parallel coplanar arrays that define ca. 21 x 6 Å "rafts". The other two chains extend on a common side of the raft, which pack back-to-back in stacks, maximizing parallel chains in every dimension. DSC shows one phase transition (melting, 2/4 75/79 °C) prior to thermal decomposition (>200 °C). The IR ν_{CO} values (2/3/4 1975/ 1942/1979 cm⁻¹) show that the CH₂CH₂ spacers do not completely insulate the metals from the perfluoroalkyl groups. Both 2 and 4 are soluble in CF₃C₆F₁₁, CF₃C₆H₅, ether, THF, and acetone, but insoluble in hexane, toluene, CHCl₃, and CH₂Cl₂ (CF₃C₆F₁₁/THF partition coefficient >99.7:<0.3). Reactions of 2 with RI, H₂, and ³O₂ or ¹O₂ in CF₃C₆F₁₁ give $\text{Ir}(\text{CO})(\text{Cl})(\text{R})(1)[\text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3)_3]_2$ (R = CH₂CH₂-(CF₂)₇CF₃/CH₃/CH(CH₃)CH₂CH₃, 5/6/7, 70-84%), $\text{Ir}(\text{CO})(\text{Cl})(\text{H})_2[\text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3)_3]_2$ (82%), and $\text{Ir}(\text{CO})(\text{Cl})(\text{O}_2)[\text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3)_3]_2$ (9, 67%), respectively. Additions of RI occur by free-radical chain mechanisms (inhibition by duroquinone; slower dark reactions; rates 7 > 5 > 6), with no evidence for polar pathways. Complex 9 forms more rapidly in THF, indicating that (relative to THF) 2 and ³O₂ are stabilized by CF₃C₆F₁₁ more than the transition state.

H. Complexes and Catalysts Immobilized in Fluorinated Solvents: Practical Methods for Catalysis (paper 95).

Fluorous solvents commonly exhibit temperature-dependent miscibilities with organic solvents. Thus, catalysts and reagents that have high affinities for fluorous solvents can be used in protocols that combine the advantages of one-phase chemistry (higher temperature) and biphasic product separation (lower temperature). This review provides a "how to" guide with respect to solvent sources, and solubility and polarity characteristics. All currently available partition coefficients for fluorous catalysts and reagents, as well as various educts and products, are tabulated.

I. Exploratory Polyoxotungstate Chemistry (paper 91).

Reaction of the chiral racemic carbonyl complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CO})]^+ \text{BF}_4^-$ and $\{(n\text{-C}_4\text{H}_9)_4\text{N}^+\}_2 [\text{W}_6\text{O}_{19}]^{2-}$ in DMF, followed by addition of CH₂Cl₂ and hexane, gives the title compound as yellow prisms (78%). A crystal structure (triclinic, P, *a*/*b*/*c* = 9.545(2)/9.687(2)/ 16.226(4) Å, $\alpha/\beta/\gamma$ = 102.46(2)/105.88(2)/87.79(2)°, *Z* = 1) shows opposite enantiomers of the cations arrayed about a dianion-based inversion center – a *meso* assembly. The enantiomerically pure carbonyl complex gives crystals with the same unit cell, but P1 space group. This is possible due to the comparable sizes of the nitrosyl and carbonyl ligands. Metrical parameters are close to those of related compounds in the literature.

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