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

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

Reaction of the amido complex \( \eta^5-C_5H_5 Re(NO)(PPPh_3)(NH_2) \) (2) and hexafluoroacetone gives the methylenemiamido complex \( \eta^5-C_5H_5 Re(NO)(PPPh_3)(N=C(CF_3)_2) \) (3, 58%). Addition of TFOH to 3 yields the \( \sigma \) imine complex \( \{\eta^5-C_5H_5 Re(NO)(PPPh_3)(\eta^1-N)(N=CH(CF_3)=CH)\}^+ \) TFO\(^-\) (4, 96%). Similar reactions of 2 with trifluoroacetaldehyde and then TFOH give the \( \sigma \) imine complex \( \{\eta^5-C_5H_5 Re(NO)(PPPh_3)(\eta^1-N)(N=CH(CF_3)=CH)\}^+ \) TFO\(^-\) (5, 78%), and sometimes small amounts of the corresponding \( \pi \) trifluoroacetaldelyde complex. Reaction of 5 and \( t-BuO^- K^+ \) gives the methylenemimido complex \( \{\eta^5-C_5H_5 Re(NO)(PPPh_3)(\eta^1-N)(N=CH(CF_3)=CH)\}^+ \) TFO\(^-\) (6, 82%). The IR and NMR properties of 3-6 are studied in detail. The \( ^13C \) NMR spectra show \( C=N \) signals (157-142 ppm) diagnostic of \( \sigma \) binding modes. No evidence is observed for \( \pi \) isomers of 4 or 5. Analogous O=C(CF_3)_2X complexes give exclusively \( \pi \) 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 \((S,R)-\eta^5-C_5H_5 Re(NO)(PPPh_3)(NHCH(CH_3)Ph)\) \((S,R)-5\) converts to \((RR)-5\) (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 \( k_2 = 0.90 \times 10^{-3} \text{s}^{-1} \). Similarly, \((SS)-5\) converts to \((RS)-5\) with \( k_1 = 0.90 \times 10^{-4} \text{s}^{-1} \) and \( k_2 = 2.30 \times 10^{-5} \text{s}^{-1} \). Both epimerizations give equilibrium ratios \((RR/SS \approx 70:30)\). Reactions with HOTf yield \( \{\eta^5-C_5H_5 Re(NO)(PPPh_3)(\eta^1-N)(N=CH(CH_3)Ph)\}^+ \) TFO\(^-\), and subsequent additions of Et_4N^+ TFO\(^-\) afford \( \{\eta^5-C_5H_5 Re(NO)(PPPh_3)(CN)\}^+ \) TFO\(^-\) and NHCH(CH_3)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 \((S,R)-5\) and P(p-tol)_3 in THF-d\(_8\) at 49.4 °C gives \( \eta^5-C_5Me_5 Re(NO)(P(p-tol)_3)(NHCH(CH_3)Ph)\) \(50:50\) \((t_0 \rightarrow 66:34) \) \((t_\infty)\) \((RR/SS)\) with \( k = 4.6 \times 10^{-4} \text{s}^{-1} \). These results are best modeled by mechanisms involving initial and rate determining PPh_3 dissociation, with anichmeric 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-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.


Reaction of \( \eta^5-C_5Me_5 Re(NO)(PPPh_3)(C=CLi) \) with Re_2(CO)_10 and then Me_3O_2^+ BF_4^- gives the trirhenium C_3OMe complex \( \text{cis}(\eta^5-C_5Me_5 Re(NO)(PPPh_3)(C=CC(O)Me)=) \) Re(CO)_4 Re(CO)_4 (3, 92%). An analogous reaction with Os_2(CO)_12 gives heterotetrametallic \( \{\eta^5-C_5Me_5 Re(NO)(PPPh_3)(C=CC(O)Me)=) \) Os_3(CO)P_1 (4, 87%). NMR, IR, and crystallographic data (4) show substantial contributions by \( ^5\text{Re}=C=C=\text{CC}(\text{OMe})=\text{Me}^- \) resonance forms. Reaction of 3 and excess BF_3 gas in toluene precipitates \( \{\eta^5-C_5Me_5 Re(NO)(PPPh_3)(\eta^1-\eta^1-N\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\·
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from 3 to give a ReCCCReRe species, followed by rearrangement. Reaction of (η⁵-C₅Me₅)-Re(NO)(PPh₃)(C≡C(OMe)=) with Re₂(CO)₁₀ and then Me₂O⁺ BF⁴⁻ gives the C₂OMe complex cis-(η⁵-C₅Me₅)Re(NO)(PPh₃)(C≡C(OMe)=)Re(CO)₄Re(CO)₅ (8, 44%). When 4 or 8 are treated with BF₃ gas, C₅ complexes are not detected.

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

Reaction of (η⁵-C₅Me₅)Re(NO)(PPh₃)(C≡C'H) and Os₃(CO)₁₀(NCC₂H₅)₂(CH₂Cl₂, RT) gives the Re₂Os₃ complex (η⁵-C₅Me₅)Re(NO)(PPh₃)(C≡C'H)Os₃(CO)₁₀(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 Re=C≡C(OMe)= and "Re=C≡C=C(O₃S)⁻ resonance forms. Analogous Re₄Os₃ (4, 83%) and ReC₅Os₃ (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 (η⁵-C₅Me₅)Re(NO)(PPh₃)(CCCC)Os₃(CO)₉(H) (57%). A crystal structure shows that the hydride and ReCC terminus binds to three osmium atoms and the adjacent carbon (and hydride) to two. Reaction of 2 and HBF₄ as Et₂O gives [(η⁵-C₅Me₅)Re(NO)(PPh₃)(CCCC)Os₃(CO)₁₀(H)₂]⁺ BF₄⁻ (69%). A crystal structure of the SbF₆⁻ salt shows a ReC₂O₃S₃ unit very similar to that of 2, with the hydrides bridging different osmium-osmium bonds. The C₂OMe complex (η⁵-C₅Me₅)Re(NO)(PPh₃)(C≡C≡C(OMe)=)Os₃(CO)₁₁ decarbonylates in refluxing heptane to give (η⁵-C₅Me₅)Re(NO)(PPh₃)(CCCCO(CO)(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 C₂ and C₅ Carbide Bridges (paper 94).

Reactions of (η⁵-C₅Me₅)Re(NO)(PPh₃)(C≡CMe) with W(CO)₆, Fe(CO)₅, or Mn(CO)₅ (η⁵-C₅H₅Cl₅-n), followed by Me₂O⁺ BF₄⁻, give the heterobimetallic C₃OMe complexes (η⁵-C₅Me₅)Re(NO)(PPh₃)(C≡CMe)W(CO)₆ (η⁵-C₅H₅Cl₅-n), (M/x/y/n = 3, 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 "Re=C≡C=C(OMe)=M" resonance forms. Reactions of 4-7 and BF₃ gas give the title complexes [(η⁵-C₅Me₅)Re(NO)(PPh₃)(CCCC)M(CO)₉(C≡CMe)]⁺ BF₄⁻ (9, W/5/0/-; 10, Mn/2/1/4; 11, Mn/2/1/0; 12, Fe/4/0/-). Spectroscopic and crystallographic (9) data indicate dominant "Re=C≡C≡C≡C≡M" resonance forms. Reactions of (η⁵-C₅Me₅)Re(NO)(PPh₃)(C≡CMe) with Mn(CO)₅ (η⁵-C₅H₅Cl₅-n), Mn(CO)₅ (η⁵-C₅H₅Br₅-n), or Fe(CO)₅, followed by Me₂O⁺ BF₄⁻, give the C₃OMe complexes (η⁵-C₅Me₅)Re(NO)(PPh₃)(C≡CMe)M(CO)₅ (M/x/y/n = 3, W/5/0/-; 4, Fe/4/0/-; 5, Mn/2/1/5; 6, Mn/2/1/4; 7, Mn/2/1/0). However, Mn(CO)₅ (η⁵-C₅H₅) does not react. Reaction of 16 and BF₃ gives the C₅ complex [(η⁵-C₅Me₅)Re(NO)(PPh₃)(CCCC)M(CO)₅(η⁵-C₅Cl₅)]⁺ BF₄⁻ (21) as a light-sensitive deep brown powder of >94% purity. IR and NMR data show a dominant "Re=C≡C≡C≡C≡M" 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 M⁻¹cm⁻¹), respectively, and weaker longer wavelength bands. These are believed to have appreciable rhenium-to-manganese charge transfer character.

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

Reactions of (η⁵-C₅R₅)Re(NO)(PPh₃)(OTf) (1a/b, R = H/Me) and (η⁵-C₅R₅)Re(NO)(PPh₃)(CN) (2a/b, R = H/Me) in toluene or CH₂Cl₂ give the title complexes (R⁻/R⁺ = H/H (4a), Me/H (4b), H/Me (4c), Me/Me (4d)) in 71-97% 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
The crystal structure of (SR,RS)-4a shows a slightly bent Re~Re linkage, bond lengths close to those of related ReN and RCRNRe compounds, and van der Waals contacts across the bridge. The diastereomers of 4a-d, and linkage isomers 4b,c, do not equilibrate in CDC13 (55 °C) or CHCl3/CHCl3 (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 [(η5-C5H5)Re(NO)(PPh3)(CH2CH=CH(CH2)2)]+ TF0- and 2a react (CHCl3/CHCl3, 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 [lr(Cl)(cod)]2, P(CH2CH2(CF2)5CF3), and CO (1 atm) gives the title compound (2, 97%). Tri[n-octyl] phophine (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 × 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 νCO values (2/3/4 1975/1942/1979 cm⁻¹) show that the CH2CH2 spacers do not completely isolate the metals from the perfluoroalkyl groups. Both 2 and 4 are soluble in CF3C6F11, CF3C6H13, ether, THF, and acetone, but insoluble in hexane, toluene, CHCl3, and CH2Cl2. The solvent partition coefficient is >99.7:<0.3. Reactions of 2 with RI, H2, and 3O2 or 1O2 in CF3C6F11 give Ir(CO)(Cl)(R)(O)1[P(CH2CH2(CF2)5CF3)1], R = CH2CH2-(CF2)7CF3/CH3/CH(CH3)2CH2CH3, 5/6/7. 70-84%, Ir(CO)(Cl)(H2)2[P(CH2CH2(CF2)5-CF3)]2 (82%), and Ir(CO)(Cl)(O2)1P(CH2CH2(CF2)5CF3)1], 9, 67%, respectively. Additions of R1 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.


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 Polyyoxotungstate Chemistry (paper 91).

Reaction of the chiral racemic carbonyl complex [(η5-C5H5)Re(NO)(PPh3)(CO)]+ BF4- and [(n-C4H9)4N+]2 [W6O19]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)/9.587(2)/16.226(4) Å, α/β/γ = 102.46(2)/105.88(2)/87.79(2)°, Z = 1) shows opposite enantiomers of the cations arrayed around 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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