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We have continued to make progress in preparing transitionmetal complexes containing fluorinated ligands, and have completed several sub-projects. We have prepared the first examples of transition metal compounds containing tetrafluoroethylene ligands that rotate rapidly on the NMR time scale. This is a significant discovery en route to a transition metal catalyst that will promote the Ziegler-Natta polymerization of fluorinated olefins to give high polymers. The factors governing the barrier to fluoroolefin rotation have been identified. We have synthesized the first example of a transition metal complex containing the pentafluorocyclopentadienyl ligand. this is an important ligand that may improve the thermal robustness of many transition metal compounds.

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FINAL TECHNICAL REPORT

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TRANSITION METAL COMPLEXES WITH PERFLUORINATED LIGANDS

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1 6 DEC 1994

Summary.

We have continued to make progress in preparing transition metal complexes containing fluorinated ligands, and have completed several sub-projects.

- We have prepared the first examples of transition metal compounds containing tetrafluoroethylene ligands that rotate rapidly on the NMR time scale. This is a significant discovery en route to a transition metal catalyst that will promote the Ziegler-Natta polymerization of fluorinated olefins to give high polymers. The factors governing the barrier to fluoroolefin rotation have been identified.

- We have synthesized the first example of a transition metal complex containing the pentafluorocyclopentadienyl ligand. This is an important ligand that may improve the thermal robustness of many transition metal compounds.

- The successful synthesis of the first pentafluorocyclopentadienyl ligand has now been followed by preparation of a second analogue, whose crystal and molecular structure has been determined. This allows for the first time a direct comparison to be made between the structural parameters of the cyclopentadienyl ligand and its perfluorinated relative.

- In order to study the oxidative stability of perfluorocyclopentadienyl complexes relative to other halogenated and non-halogenated cyclopentadienyl ligands, we have now completed detailed UV photoelectron spectra studies which allow a detailed comparison of the electronic structure of fluorine, chlorine, and hydrogen substituents on the cyclopentadienyl ring.

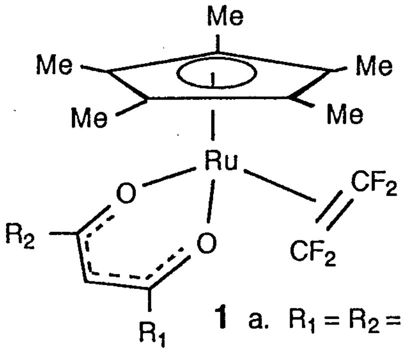
- We have also completed the synthesis of the first series of compounds containing partially fluorinated cyclopentadienyl rings. Every isomer of $C_5F_nH_{5-n}$ has been prepared in a completely selective manner.

- We have also completed the synthesis and characterization of the first transition metal complex containing an η^4–ligated hexafluorobutadiene ligand, allowing for the first time a detailed comparison of the structural parameters of η^4–butadiene and its perfluorinated relative.

A New Approach to Transition Metal Catalyzed Polymerization of Fluoro-olefins.

The Ziegler-Natta polymerization of hydrocarbon olefins is well known. The reaction is thought to proceed by stepwise binding of an olefin to a metal in a position adjacent to a metal–C σ-bond, followed by migratory insertion of the olefin via a four-center coplanar transition state to generate a new M– σ-bond and a vacant coordination site for binding a new molecule of olefin. Model organometallic systems have been developed which mimic the chain growth step of this reaction.[1] Even though tetrafluoroethylene (TEFLON) is an important industrial material, it cannot be prepared by transition metal catalyzed routes, and other fluoro-olefin analogues of TEFLON are almost unknown. There are no known examples of insertion of a fluoro-olefin into a metal–C or even a metal–F bond.[2] There appear to be two serious constraints in the systems which have been available for study to date. The metal-fluoroalkyl bond is thought to be strong, and the metal-fluoroolefin bond is also strong, due to significant back-bonding from the metal-d into olefin-π^*.[2] Thus the fluoroolefin is conformationally rigid, and cannot easily undergo propeller rotation about the metal-olefin axis into the correct conformation required for insertion. The activation energy barriers to propeller rotation for many hydrocarbon olefin complexes have been measured using NMR techniques.[1] Most such rotations are fast on the NMR time scale. There are no reported compounds containing a rotationally dynamic tetrafluoroethylene ligand.[2] In all cases back-bonding appears to be strong enough to lock the fluoro-olefin in one conformation and preclude any further chemistry.

We have prepared the first family of compounds in which tetrafluoroethylene rotates freely on the NMR time scale at room temperature. For example, compound **1a** shows two strongly coupled F environments which are 10 ppm apart at –50°C, but which coalesce to a single F environment at +50°C. The large chemical shift separation of the two environments indicated that in order to observe coalescence, propeller rotation of the fluoroolefin must have a very small activation energy. This barrier has now been measured to be 12-13 kcal. mol^{-1}.[3] In order to evaluate the factors affecting the metal-fluoroolefin bonding, the magnitude of the barriers in a series of compounds **1** has been measured by NMR techniques, and correlated with computational calculations at the Extended Hückel level on the electronic structure of the complex.[4] Clearly the combination of metal, oxidation state, and ancillary ligands has finally been found in which the back bonding interaction is sufficient to allow binding but insufficient to preclude rotation. We have discovered the first perfluoroolefin which behaves like a hydrocarbon olefin when bound to a metal center! We are continuing to explore the chemistry of these systems with a view to assembling a metal complex in which insertion of a fluoroolefin into a metal–C bond can be achieved, substantially enhancing the prospects for observing a fluorinated analogue of Ziegler-Natta catalysis.



1 a. $R_1 = R_2 = CH_3$

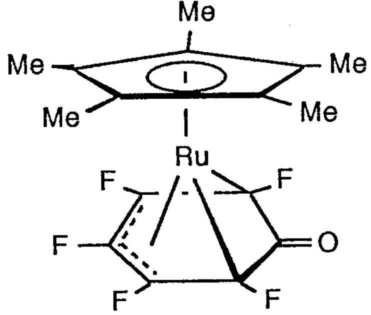
b. $R_1 = R_2 = CF_3$

c. $R_1 = CH_3$; $R_2 = CF_3$

Fluorinated Cyclopentadienyl Ligands.

Transition metal complexes containing the perfluorocyclopentadienyl ligand should be compounds of enhanced thermal stability compared to their hydrocarbon analogues.[1] The problem is a synthetic one; direct methods for fluorinating cyclopentadienyl rings are inefficient at best, and at worst are incompatible with the relatively low oxidation potentials of many transition metal centers. An indirect method is necessary.

Our successful method forms metal-carbon linkages first, before extruding a small gaseous molecule of CO to obtain the perfluorocyclopentadienyl ring. We have synthesized complex **2** from the reaction of $[Ru(C_5Me_5)Cl]_4$ with $TlOC_6F_5$.[5] Thermal extrusion of CO by flash vacuum pyrolysis at 770°C affords the desired complex $[Ru(C_5Me_5)(C_5F_5)]$ (**3**).[5] The successful synthesis of this compound was viewed as significant enough in this country and in Europe to be included in the Science and Technology Concentrates in the U.S. publication Chemical & Engineering News,[6] and also in the German Annual Review of Inorganic Chemistry (Jahresrückblick Anorganische Chemie).[7]



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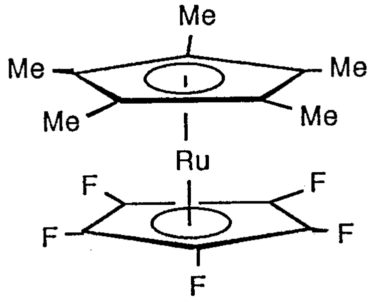

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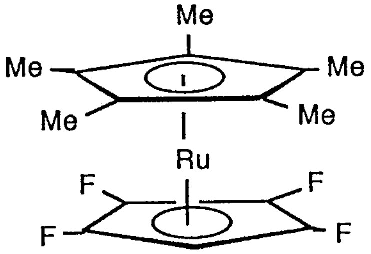
This method is general for the pentamethylcyclopentadienyl-ruthenium fragment, and we have now succeeded in preparing all the isomers of partially fluorinated cyclopentadienyl ligands by this route: i.e. $[Ru(C_5Me_5)(C_5F_4H)]$ (**3**), $[Ru(C_5Me_5)(C_5F_3H_2)]$ (1,2,3-, and 1,2,4-isomers, **4** and **5**), $[Ru(C_5Me_5)(C_5F_2H_3)]$ (1,3- and 1,2 isomers, **6** and **7**), and $[Ru(C_5Me_5)(C_5FH_4)]$ (**8**), can all be prepared selectively from the corresponding fluorinated phenols.[8] The molecular structures of **8** and **9** have been determined by X-ray crystallography.[8]



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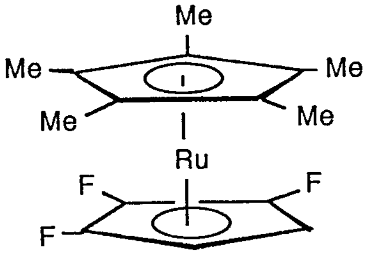

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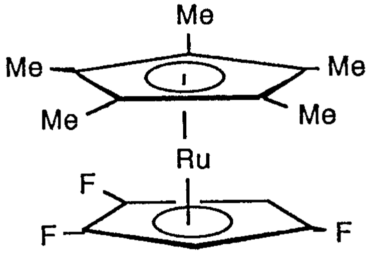

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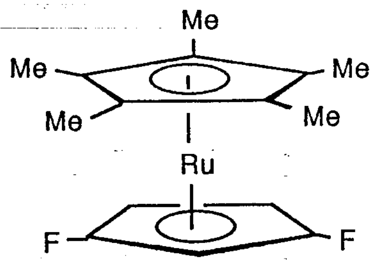

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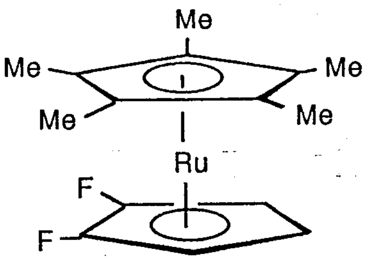

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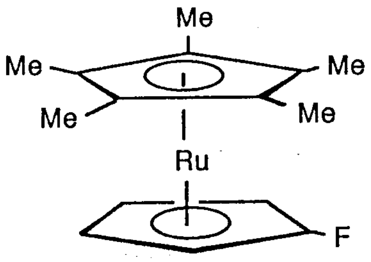

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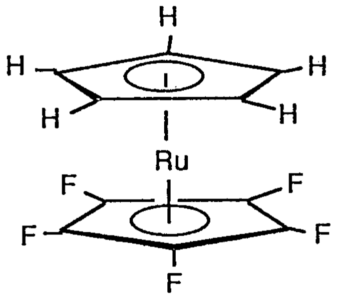
We have also completed a study with Professor David Richardson of the gas phase ionization energy of **3** in comparison with the corresponding pentahydrogen, pentamethyl, and pentachloro analogues.[9] These studies indicate that the F substituent is similar to the Cl substituent in transmission of electronic effects to the metal center, though of course the C–F bond energy is considerably greater than the C–Cl energy. We have been unable thus far to obtain reversible redox behavior in the solution phase.[9] A complementary study of the gas phase UV photoelectron spectra of **3** and its pentahydrogen and pentachloro analogues has now also been completed with Professor Dennis Lichtenberger.[10] The studies has mapped the orbital energy levels on the metal center, and provides a more detailed rationale of the transmission of electronic effects of substituents to the ruthenium.

We have been finally prepared the unsubstituted parent ruthenium analogue $[Ru(C_5H_5)(C_5F_5)]$ (**10**) via a similar synthetic route, and determined its molecular structure by X-ray crystallography.[11] The structure shows, as expected, a significantly stronger interaction between the metal and the fluorinated ring.



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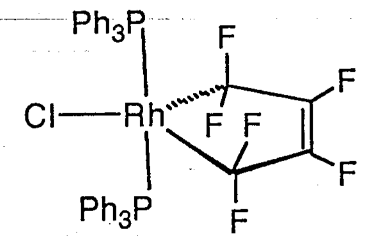
Transition Metal Chemistry of Hexafluorobutadiene.

We have begun a study of the transition metal chemistry of hexafluorobutadiene, with the intent of developing catalysts to polymerize this monomer. We have succeeded in preparing the metallacyclic complexes **11** and **12** and have shown that while the coordinatively saturated complex **12** is quite stable, its 16-electron analogue **11** undergoes an astonishingly facile hydrolysis reaction of one CF_2 group to afford **14**. We do not understand why the second CF_2 group does not undergo a similar hydrolysis.[12]



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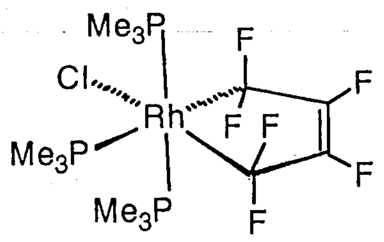

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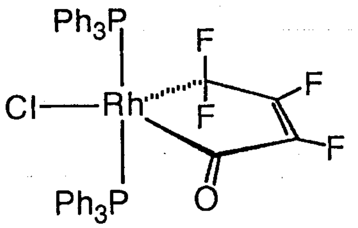
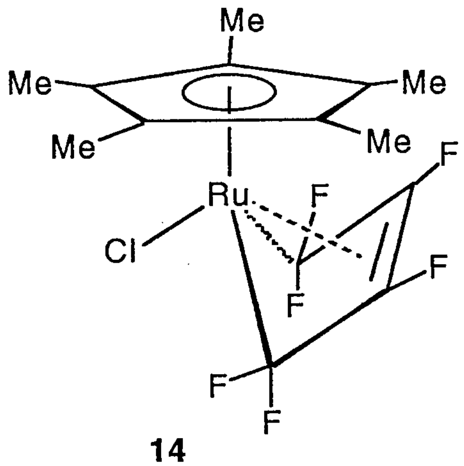


13

We have finally succeeded in preparing the first example of an η^4–complex of hexafluorobutadiene (**14**), and have determined its X-ray structure.[13] The structure provides the first comparison of the bonding of this perfluorinated diene with its more well known hydrocarbon relative, butadiene, in the known complex **15**. The fluorinated diene binds in a manner best depicted by the drawing shown in **14** while the hydrocarbon prefers the mode shown in **15**. The factors influencing these differences in bonding have been examined and will be published shortly.[13]



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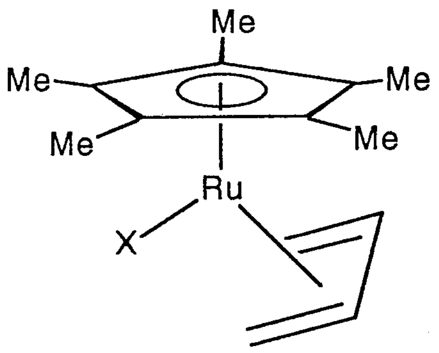

15 a. X = Cl
b. X = I

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Co-workers On the Project.

Postdoctoral Associates:	Dr. Owen J. Curnow (Ph.D. University of Michigan)
	Dr. Demetrakis Loizou (Ph.D. University of Illinois at Chicago)
Graduate Students:	Peter Rose
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	Danielle Progno
Undergraduate Students:	Erin N. Mairs
	Christopher A. Morse
	Christina R. Kahl
External Collaborators:	Professor William Geiger (Vermont): Electrochemistry
	Professor Dennis Lichtenberger (Arizona): Photoelectron Spectroscopy
	Professor David Richardson (Florida): Gas Phase Ionization
	Professor Arnold Rheingold (Delaware): X-ray Crystallography

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Cumulative List of Papers Acknowledging AFOSR Support: 1992–1995

1. **O.J. Curnow, R.P. Hughes, and A.L. Rheingold**
An (η^2–Tetrafluoroethylene)ruthenium Complex with a
Metallacyclopropane Structure but with a Low Barrier to Propellor Rotation
J. Am. Chem. Soc., 1992, <u>114,</u> 3153.

2. **O.J. Curnow and R.P. Hughes**
[Ru(η^5–C_5Me_5)(η^5–C_5F_5): The First Transition Metal Complex Containing a
Perfluorocyclopentadienyl Ligand
J. Am. Chem. Soc., 1992, <u>114,</u> 5895.

3. **D.E. Richardson, M.F. Ryan, W.E. Geiger, T.T. Chin, R.P. Hughes, and O.J. Curnow**
Gas-Phase and Solution Studies of the Oxidation of the
First Perfluorocyclopentadienyl Complex [Ru(η^5–C_5Me_5)(η^5–C_5F_5)]
Organometallics, 1993, <u>12,</u> 613.

4. **O.J. Curnow, R.P. Hughes, E.N. Mairs, and A. L. Rheingold**
Facile Propeller Rotation in Metallacyclopropanes.
Synthesis and Dynamic Behavior of New Tetrafluoroethylene–Ruthenium Complexes.
Crystal and Molecular Structure of [Ru(η^5–C_5Me_5)Cl(η^2–C_2F_4)]$_2$
Organometallics, 1993, <u>12,</u> 3102.

5. **R.P. Hughes, P.R. Rose, and A. L. Rheingold**
Transition Metal Chemistry of Hexafluorobutadiene. Facile Hydrolysis of
Hexafluoro-1-metalla-3-cyclopentene Rhodium Complexes to give
Tetrafluoro-1-metalla-3-cyclopentene-2-one and Tetrafluoro-1-metalla-2-cyclopentene-4-one
Complexes. Crystal and Molecular Structures of trans–[(Rh–CF_2CF=CF–CO)Cl(PPh_3)$_2$],
mer–[(Rh–CF_2CF=CF–CF_2)Cl(PMe_3)$_3$], and mer–[(Rh–CF=CF–CO–CF_2)Cl(PMe_3)$_3$]
Organometallics, 1993, <u>12,</u> 3109.

6. **R. P. Hughes and D. S Tucker**
η^3–Cyclopropenyl is Isolobal with NO, but not with η^3–Propenyl (Allyl):
Evidence from Conformational Preferences and Rotational Barriers in
Alkene and Alkyne Complexes of Iridium.
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7. **R. P. Hughes, X. Zheng, R. L. Ostrander, and A. L. Rheingold**
Synthesis and Molecular Structure of [Ru(η^5–C_5H_5)(η^5–C_5F_5)].
Intramolecular Structural Comparison of the Cyclopentadienyl Ligand
with its Perfluorinated Analogue.
Organometallics, 1994, 13, 1567.

8. **R. P. Hughes, O. J. Curnow, E.N. Mairs, P. R. Rose, X. Zheng, and A. L. Rheingold**
New and Revisited Transition Metal Chemistry of Fluoro-Olefins and Fluoro-Dienes
Adv. Chem. Ser., 1994, 515, 252.

9. **R.P. Hughes, P. R. Rose, X. Zheng, and A. L. Rheingold**
Synthesis and Molecular Structure of the First Example of an η^4–Complex of
Hexafluorobutadiene: [RuCl(η^5–C_5Me_5)(η^4–C_4F_6)]. Structural Comparison of
Coordinated Butadiene and its Perfluorinated Analogue.
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