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COMPLETED PROJECT SUMMARY

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Department of Chemistry
Dartmouth College
Hanover NH 03755
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R.P. Hughes, R.T. Carl, R.C. Hemond, D.E. Samkoff, and A.L. Rheingold,
Unprecedented Coordination of a Cyclooctatetraene Ligand. Synthesis and Crystal and Molecular Structure of (η -Pentamethylcyclopentadienyl)(1,4- η -octafluorocyclooctatetraene)(trimethylphosphine)rhodium(III).
J. Chem. Soc. Chem. Commun., 1986, 306.

R.P. Hughes, R.T. Carl, D.E. Samkoff, R.E. Davis, and K.D. Holland,
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J. Phys. Chem., 1987, **91**, 6168.

R.T. Carl, R.P. Hughes, J.A. Johnson, R.E. Davis, and R. Kashyap,
Unprecedented Bonding of a Coordinated Polyenyl Ligand.
Synthesis and Molecular Structures of *fac*-(Trialkyl)(tricarbonyl)iron Compounds
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J.J. Bel Bruno, S.R. Greenfield, R.T. Carl, and R.P. Hughes,
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J. Phys. Chem., 1988, **92**, 2480.

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Synthesis, Structures, and Solution Dynamics of Mononuclear and Dinuclear η^5 -Indenylrhodium
Complexes of Octafluorocyclooctatetraene. Crystal and Molecular Structures of
[Rh(η^5 -C₉H₇)(1,2,5,6- η -C₈F₈)], {[Rh(η^5 -C₉H₇)]₂[μ -(1,5,6- η :2-4- η -C₈F₈)](*Rh-Rh*)},
[Rh(η^5 -C₉H₇)]₂[μ -(1,5,6- η :2-4- η -C₈F₇H)](*Rh-Rh*)}, and
[Rh(η^5 -C₉H₇)(CO)][Rh(η^5 -C₉H₇)] [μ -(1,2,5,6- η :7,8- η -C₈F₈)].
Organometallics, 1988, **7**, 1613.

R.T. Carl, R.P. Hughes, and D.E. Samkoff
Transannular Ring-Closure Reactions of Octafluorocyclooctatetraene Coordinated to Cobalt and
Rhodium Centers.
Exogenous Ligand Induced Formation of η^2 -Octafluorocycloocta-2,5,7-triene-1,4-diyl and
 η^2 -Octafluorobicyclo[3.3.0]octa-2,7-diene-4,6-diyl Complexes of Cobalt(III) and Rhodium(III).
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R.C. Hemond, R. P. Hughes, D. J. Robinson, and A. L. Rheingold
Activation of a Fluorinated Carbon-Carbon Bond by Oxidative Addition of Tetrafluorocyclopropene
to Platinum(0).
The First Example of a Perfluorometallacyclobutene.
Organometallics, 1988, **7**, 2239.

R. P. Hughes, J. Robbins, D. J. Robinson, and A. L. Rheingold
Conformationally Rigid η^3 -Cyclopropenyl Complexes of Ruthenium(IV).
Crystal and Molecular Structure of [Ru(η^5 -C₅H₅)(η^3 -C₃Ph₃)Br₂].
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R.C. Hemond, R.P. Hughes, and A.L. Rheingold,
Synthesis of η^6 -Octafluorocyclooctatetraene and η^6 -Cyclooctatetraene Complexes of
Manganese(I). Molecular Structures of [Mn(η^5 -C₅R₅)(η^6 -C₈X₈)] (R = H, Me; X = F; R = Me; X = H).
Organometallics, 1989, **8**, 1261.

R.P. Hughes, M.E. King, D.J. Robinson, and J.M. Spotts

Stereoselective Oxidative Additions of a Carbon-Carbon σ -Bond in Tetrafluorocyclopropene to Iridium(I) Complexes.

J. Am. Chem. Soc., 1989, **111**, 8919.

R.T. Carl, E.W. Corcoran Jr, R.P. Hughes, and D.E. Samkoff

Nickel, Palladium, and Platinum Complexes Derived From Octafluorocyclooctatetraene.

Synthesis of 1,2,5,6- η -Octafluorocyclooctatetraene Complexes of Nickel(0) and

η^2 -Octafluorobicyclo[3.3.0]octa-2,7-diene-4,6-diyl Complexes of Nickel(II), Palladium(II) and Platinum(II) *Organometallics*, 1990, **9**, 0000.

R.P. Hughes

Organo-Transition Metal Chemistry with Perfluorinated Ligands:

Octafluorocycloocta-1,3,5,7-tetraene (OFCOT), and its Valence Isomers

Adv. Organomet. Chem., 1990, In the press.

R.P. Hughes, R.T. Carl, S.J. Dolg, R.C. Hemond, D. E. Samkoff, W.L. Smith, L.C.

Stewart, R.E. Davis, H.K. Ashbaugh, P. Dickens, and R.P. Kashyap

Effect of Polyfluorination on Ring Inversion Barriers for Cyclooctatetraenes.

Synthesis of Heptafluorocycloocta-1,3,5,7-tetraenyl, Hexafluorocycloocta-1,3,5,7-tetraenediyl,

Heptafluorotricyclo[4.2.0.0^{2,5}]octa-3,7-dienyl, and Hexafluorotricyclo[4.2.0.0^{2,5}]octa-3,7-diendiyl

Transition Metal Compounds. Crystal and Molecular Structures of

[Fe(η -C₅R₅)(η^1 -Heptafluorocycloocta-1,3,5,7-tetraenyl)(CO)₂] {R = H, Me},

{[Fe(η -C₅H₅)(CO)₂]₂(μ_2 -1 η ,5 η -Hexafluorocycloocta-1,3,5,7-tetraenediyl)}, and

[Mn(3 η -Heptafluorotricyclo[4.2.0.0^{2,5}]octa-3,7-dienyl)(CO)₅].

J. Am. Chem. Soc. submitted for publication.

R.P. Hughes, S.J. Dolg, R.C. Hemond, W.L. Smith, R.E. Davis, S.M. Gadol, K.D.

Holland, and R.P. Kashyap

Synthesis, Structures, and Conformational Dynamics of Dicobalt Complexes

Containing the Hexafluorodehydrocyclooctatetraene (Hexafluorocycloocta-3,5,7-trien-1-yne) Ligand.

Crystal and Molecular Structures of

[(Co(L)(CO)₂)₂(μ_2 -1 η ,2 η -C₈F₆)] {L = CO, PPh₃, PPhMe₂, PMe₃}.

J. Am. Chem. Soc. submitted for publication.

8. ABSTRACT OF ACCOMPLISHMENTS AND OBJECTIVES:

The principal objective of this program was to evaluate the scope of the transition metal chemistry of perfluorinated ligands, with emphasis on octafluorocyclooctatetraene (OFCOT). New coordination modes for OFCOT bound to rhodium, cobalt, nickel, palladium, platinum, and manganese have been discovered, some of which have no precedent in hydrocarbon chemistry, and all complexes show enhanced air and thermal stability compared to hydrocarbon analogues. Photochemical rearrangements of cobalt and rhodium OFCOT complexes have been discovered, and unprecedented transannular ring closure chemistry of coordinated OFCOT has also been revealed. Comparison of the bonding properties of OFCOT with those of its hydrocarbon analogue has been achieved using crystallographic and NMR studies, and comparisons of the multiphoton ionization processes of iron complexes of OFCOT and its hydrocarbon analogue have been made. An iron complex of OFCOT has been shown to react with nucleophiles to generate the first examples of a new family of (trialkyl(tricarbonyl) organometallic compounds, stabilized by tridentate perfluorinated ligands. Dinuclear rhodium complexes of OFCOT have been prepared, and shown to undergo a very selective C-F bond activation reaction. Electrochemical reduction of OFCOT bound to cobalt has been shown to yield the first example of a fluorinated organometallic radical anion. Metal substitution on the OFCOT ring has also been achieved, and the resultant compounds have allowed a quantitative study of the effect of fluorination on the conformational dynamics of cyclooctatetraenes to be carried out. Vicinal defluorination of OFCOT by cobalt

complexes has allowed the synthesis and characterization of a series of compounds containing the previously unknown μ -hexafluorocyclooctatrieneyne ligand. A remarkably facile cleavage of a fluorinated C-C bond σ -bond in perfluorocyclopropene by platinum and iridium complexes has been achieved. The cleavage by iridium has been shown to be stereospecific at the metal center, the first time such stereospecificity has been demonstrated for a C-C cleavage reaction.

FINAL REPORT

JANUARY 1, 1986 - AUGUST 31, 1989

GRANT AFOSR-86-0075

PERFLUORINATED LIGANDS IN ORGANOMETALLIC CHEMISTRY

Principal Investigator:

Russell P. Hughes,
Department of Chemistry,
Dartmouth College,
Hanover,
NH 03755

Objectives.

The principal objective of this research program was to evaluate the scope of the transition metal chemistry of perfluorinated ligands. The bulk of our work has concentrated on the ligand, octafluorocyclooctatetraene (OFCOT), and the list of published papers and manuscripts in press or submitted, which is included at the end of this report, attests to our success. In particular, the work in this area is now the subject of an extensive solicited review, which will appear in *Advances in Organometallic Chemistry* in 1990¹⁸.

We have uncovered numerous novel ligation modes and chemical reactivity for OFCOT, some of which have no precedent in the organometallic chemistry of its hydrocarbon analogue. Only a brief survey of these results is included in the following paragraphs, since the details appear in the attached reprints and in previous technical reports.

RESULTS.

1. OFCOT Chemistry and Reactivity.

Novel coordination modes for OFCOT bound to rhodium^{1,5,11,12}, cobalt^{5,12}, nickel,^{2,17} palladium¹⁷, platinum¹⁷, and manganese¹⁵ have been discovered. The manganese complexes $[\text{Mn}(\eta^5\text{-C}_5\text{R}_5)(\eta^6\text{-OFCOT})]$ show enormously enhanced air and thermal stability compared to their direct hydrocarbon analogues¹⁵, as do all the OFCOT complexes which we have prepared. Novel photochemical rearrangements of cobalt and rhodium OFCOT complexes have been discovered⁵, and unprecedented transannular ring closure chemistry of coordinated OFCOT has also been uncovered^{2,12,17}.

A direct comparison of the bonding properties of OFCOT with those of its hydrocarbon analogue has been achieved using crystallographic and NMR studies¹¹, and comparisons of the multiphoton ionization processes of iron complexes of OFCOT and its hydrocarbon analogue have been made^{7,9}.

An iron complex of OFCOT has been shown to react with both hard and soft nucleophiles to generate the first examples of a new family of (trialkyl(tricarbonyl) organometallic compounds⁸, which are stabilized by tridentate perfluorinated ligands.

Dinuclear rhodium complexes of OFCOT have been prepared, and shown to undergo a very selective C-F bond activation reaction¹¹.

Electrochemical reduction of OFCOT bound to cobalt has been shown to yield the first example of a fluorinated organometallic radical anion⁵.

Metal substitution on the OFCOT ring has also been achieved, and the resultant compounds have allowed a quantitative study of the effect of fluorination on the conformational dynamics of cyclooctatetraenes to be carried out¹⁹. A vicinal defluorination of OFCOT by cobalt carbonyl complexes has allowed the synthesis and characterization of a series of compounds containing the

previously unknown μ -hexafluorocyclooctatrieneyne ligand²⁰.

2. Vinylcyclopropene Chemistry.

In order to probe the feasibility of using fluorinated vinylcyclopropenes as precursors to the unknown η^5 -pentafluorocyclopentadienyl complexes of the transition metals, the reactions of some hydrocarbon analogues have been investigated. These reactions do indeed afford cyclopentadienyl complexes⁶, but extensions to a partially fluorinated analogue instead led to a cyclobutadiene skeleton, rather than the desired five membered ring¹⁰. This suggests that perfluorovinylcyclopropene may not be a useful precursor to pentafluorocyclopentadienyl complexes, although we still plan to study its chemistry in view of results presented in the following paragraph.

3. Activation of Fluorinated C-C Bonds.

A remarkably facile cleavage of a fluorinated C-C bond σ -bond in perfluorocyclopropene by platinum and iridium complexes has been achieved^{13,16}. The cleavage by iridium has been shown to be stereospecific at the metal center, the first time such stereospecificity has been demonstrated for a C-C cleavage reaction¹⁶.

4. Serendipitous Discoveries.

While repeating a literature preparation for some starting materials needed for subsequent OFCOT chemistry, we discovered that the literature report was incorrect, and serendipitously uncovered a competitive activation between allylic C-H and C-C bonds of pentamethylcyclopentadiene by manganese³.

Co-workers On the Project

<i>Postdoctoral Associates:</i>	Dr. James W. Egan, Jr.	(Ph.D. University of West Virginia)
	Dr. William P. Henry	(Ph.D. University of Nebraska)
	Dr. David J. Robinson	(Ph.D. University of South Africa)
	Dr. Deborah E. Samkoff	(Ph.D. University of Illinois)
<i>Graduate Students:</i>	Richard T. Carl	
	Richard C. Hemond	
	Peter Rose	
<i>Undergraduate Students:</i>	Edward W. Corcoran Jr.	
	Jocelyn A. Johnson	
	Mackenzie E. King	
	Jennifer Robbins	
	James M. Spotts	
	Leslie C. Stewart	

Cumulative List of Papers Acknowledging AFOSR Support.

1. **R.P. Hughes, R.T. Carl, R.C. Hemond, D.E. Samkoff, and A.L. Rheingold,**
Unprecedented Coordination of a Cyclooctatetraene Ligand. Synthesis and Crystal and Molecular Structure of (η -Pentamethylcyclopentadienyl)(1,4- η -octafluorocyclooctatetraene)(trimethylphosphine)rhodium(III).
J. Chem. Soc. Chem. Commun., 1986, 306.
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J. Am. Chem. Soc., 1986, 108, 7862.
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Organometallics, 1988, 7, 1613.

12. **R.T. Carl, R.P. Hughes, and D.E. Samkoff**
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13. **R.C. Hemond, R. P. Hughes, D. J. Robinson, and A. L. Rheingold**
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14. **R. P. Hughes, J. Robbins, D. J. Robinson, and A. L. Rheingold**
Conformationally Rigid η^3 -Cyclopropenyl Complexes of Ruthenium(IV).
Crystal and Molecular Structure of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\eta^3\text{-C}_3\text{Ph}_3)\text{Br}_2]$.
Organometallics, 1988, 7, 2413.

15. **R.C. Hemond, R.P. Hughes, and A.L. Rheingold,**
Synthesis of η^6 -Octafluorocyclooctatetraene and η^6 -Cyclooctatetraene Complexes of Manganese(I). Molecular Structures of $[\text{Mn}(\eta^5\text{-C}_5\text{R}_5)(\eta^6\text{-C}_8\text{X}_8)]$ ($\text{R} = \text{H, Me; X} = \text{F; R} = \text{Me; X} = \text{H}$).
Organometallics, 1989, 8, 1261.

16. **R.P. Hughes, M.E. King, D.J. Robinson, and J.M. Spotts**
Stereoselective Oxidative Additions of a Carbon-Carbon σ -Bond in Tetrafluorocyclopropene to Iridium(I) Complexes.
J. Am. Chem. Soc., 1989, 111, 8919.

17. **R.T. Carl, E.W. Corcoran Jr, R.P. Hughes, and D.E. Samkoff**
Nickel, Palladium, and Platinum Complexes Derived From Octafluorocyclooctatetraene. Synthesis of 1,2,5,6- η -Octafluorocyclooctatetraene Complexes of Nickel(0) and η^2 -Octafluorobicyclo[3.3.0]octa-2,7-diene-4,6-diyl Complexes of Nickel(II), Palladium(II) and Platinum(II)
Organometallics, 1990, 9, 0000.

18. **R.P. Hughes**
Organo-Transition Metal Chemistry with Perfluorinated Ligands: Octafluorocycloocta-1,3,5,7-tetraene (OFCOT), and its Valence Isomers
Adv. Organomet. Chem., 1990, in the press.

19. **R.P. Hughes, R.T. Carl, S.J. Dolg, R.C. Hemond, D. E. Samkoff, W.L. Smith, L.C. Stewart, R.E. Davis, H.K. Ashbaugh, P. Dickens, and R.P. Kashyap**
 Effect of Polyfluorination on Ring Inversion Barriers for Cyclooctatetraenes.
 Synthesis of Heptafluorocycloocta-1,3,5,7-tetraenyl, Hexafluorocycloocta-1,3,5,7-tetraenediyl,
 Heptafluorotricyclo[4.2.0.0^{2,5}]octa-3,7-dienyl, and Hexafluorotricyclo[4.2.0.0^{2,5}]octa-3,7-diendiyl
 Transition Metal Compounds. Crystal and Molecular Structures of
 $[\text{Fe}(\eta\text{-C}_5\text{R}_5)(\eta^1\text{-Heptafluorocycloocta-1,3,5,7-tetraenyl})(\text{CO})_2]$ $\{\text{R} = \text{H, Me}\}$,
 $\{[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]_2(\mu_2\text{-}\eta^1,5\eta\text{-Hexafluorocycloocta-1,3,5,7-tetraenediyl})\}$, and
 $[\text{Mn}(3\eta\text{-Heptafluorotricyclo[4.2.0.0}^{2,5}\text{]octa-3,7-dienyl})(\text{CO})_5]$.
J. Am. Chem. Soc. submitted for publication.

20. **R.P. Hughes, S.J. Dolg, R.C. Hemond, W.L. Smith, R.E. Davis, S.M. Gadol, K.D. Holland, and R.P. Kashyap**
 Synthesis, Structures, and Conformational Dynamics of Dicobalt Complexes
 Containing the Hexafluorodehydrocyclooctatetraene (Hexafluorocycloocta-3,5,7-trien-1-yne) Ligand.
 Crystal and Molecular Structures of $[(\text{Co}(\text{L})(\text{CO})_2)_2(\mu_2\text{-}\eta^1,2\eta\text{-C}_8\text{F}_6)]$ $\{\text{L} = \text{CO, PPh}_3, \text{PPhMe}_2, \text{PMe}_3\}$.
J. Am. Chem. Soc. submitted for publication.