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Editorial

This issue of the *Journal of Fluorine Chemistry* honors Russell P. Hughes, the winner of the 2010 American Chemical Society Award for Creative Work in Fluorine Chemistry. Born in 1946 in Denbigh, Wales, Hughes received his undergraduate education at the University of Manchester Institute of Science and Technology in England and his Ph.D. with John Powell at the University of Toronto. Postdoctoral fellowships followed with Michael Green at the University of Bristol in England, then with John Harrod at McGill University in Montreal. In 1976 he joined the Dartmouth College Chemistry Department in New Hampshire, where he is now the Frank R. Mori Professor of Chemistry.

Professor Hughes is the world leader in the field of fluorocarbon transition metal chemistry. Salient features of his research on fluorinated complexes of 13 transition metals include the invention of clever synthetic methods, thorough and insightful structural analysis, and elegant mechanistic investigations. The many firsts achieved by the Hughes group include the first perfluorometallocyclobutene, first η^4-perfluorobutadiene compound, first perfluorobutatriene complex, first perfluorobenzyne complex, and first bis(trifluoromethyl)carbene complex. Especially noteworthy are the first perfluorocarbyne (CF) complexes and the long-sought first complexes of the perfluorocyclopentadienyl ligand, discussed below.

Early on, Hughes pioneered the transition metal chemistry of perfluorocyclooctatetraene, which yielded a cornucopia of fascinating structures and transformations presented in a series of 18 papers. Not surprisingly, sharp contrasts were found with the transition metal chemistry of the parent hydrocarbon. Remarkable structural diversity characterizes the large array of complexes that were created, some of which incorporate novel bonding features. Studies of thermal and photochemical rearrangements and of conformational dynamics complement the synthetic and structural work in this series.

Given the ubiquity of cyclopentadienyl and substituted cyclopentadienyl ligands in organometallic chemistry, together with the ability of fluoro substituents to modify properties and reactivity, there was great interest among organometallic chemists in obtaining complexes of the perfluorocyclopentadienyl ligand. Seppelt was successful in synthesizing the perfluorocyclopentadienide anion and its conjugate acid, but unlike the parent species, neither served as a precursor for transition metal complexes. A variety of approaches have been employed to create substituted cyclopentadienyl ligands, but Hughes had to invent a novel one to solve this thorny problem. In 1992, from pentafluorophenol he was able to prepare a Cp* complex of ruthenium bearing an η^5-pentafluorooxocyclohexadienyl ligand. Flash vacuum pyrolysis of this compound resulted in decarbonylation and formation of $[\mathrm{Ru}(\eta^5\text{-Cp}^*)(\eta^5\text{-C}_5\mathrm{F}_5)]$. Employing the same synthetic methodology, Hughes synthesized the complete set of partially fluorinated analogues of this complex. In collaborative studies, the nature of these structures was probed using cyclic voltammetry, gas-phase electron-transfer equilibria, and density functional calculations. The Cp analogue of this Cp* compound was prepared and its crystal structure determined. The ingenuity and thoroughness of this phase of Hughes's work is characteristic of his entire research program.

In recent years, carbon-fluorine bond activation has been a major theme of his research. Recognizing the global warming potential of perfluorocarbons, he has been developing methodology using transition metal compounds to replace normally inert aliphatic C–F bonds with C–H and C–C bonds. The goal is stoichiometric and ultimately catalytic methods for transforming perfluorocarbons and other halofluorocarbons on a large scale into hydrofluorocarbons, compounds that contribute little to global warming because of their short atmospheric lifetimes. Earlier exploration of hydrolysis by bound water of the α-CF_2 groups of perfluoroalkyl ligands bound to iridium led in 1999 to the first examples of hydrogenolysis of those groups using dihydrogen under ambient conditions. A perfluoroethyl ligand, for example, was transformed into HFC-134a, replacement refrigerant for CFC-12. The Hughes group subsequently found that, analogously to hydrogen, metal-bound alkyl, aryl, alkenyl and alkynyl groups can migrate to carbon after loss of fluoride, and that these reactions occur with complete diastereoselectivity. To meet the very tough mechanistic challenge these transformations presented, Hughes brought to bear isotopic labeling, intermediate trapping, and $^{19}\mathrm{F}\{^1\mathrm{H}\}$HOESY plus DNMR experiments, together with a sophisticated kinetic study. This work showcased his skill in wielding the tools of the physical organic chemist.

The research discussed here is just a sample of a very large body of work in fluoroorganic transition metal chemistry. The Hughes group has also investigated π-stacking of fluorocarbons with hydrocarbons, engaged in fluorous chemistry, and both created and studied numerous fluoroalkyl, fluoraryl and fluorocarbene complexes of transition metals ranging from manganese to platinum. Computational chemistry now plays a key role in Hughes's research. He has employed density functional theory very effectively for guidance with experimental design, assistance with interpretation of experimental results, and determination of bond energies.

Hughes has been a Fellow of the Alfred P. Sloan and Alexander von Humboldt Foundations. He was awarded the degree of Doctor of Science by the University of Manchester, and is a Fellow of the

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Royal Society of Chemistry and a Chartered Chemist (UK). A member of the Editorial Advisory Boards of *Organometallics* and the *Journal of Fluorine Chemistry*, Hughes is co-author of more than 175 publications in organometallic chemistry. He has been a member of the Executive Committee of the Fluorine Division and has served as Chair of both the Organometallic Subdivision of the American Chemical Society and the Organometallic Gordon Research Conference. Renowned among Dartmouth students for his teaching, Professor Hughes is in his element whether the subject is general, inorganic, organometallic, or organic chemistry. Receiving Dartmouth's ''Profiles in Excellence'' Teaching Award was an honor he particular values.

Congratulations to Russ Hughes for his multifaceted contributions to chemistry, and best wishes for his chemical future.