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The first examples of perfluorobenzyl complexes of the transition metals have been prepared. Several complexes were characterized by X-ray crystallography, and the bond from the perfluorobenzyl ligand to cobalt, rhodium, and iridium appears to be unusually weak. While the perfluorobenzyl ligand in several cobalt complexes was shown to be unusually reactive towards coupling with ancillary ligands like pentamethylcyclopentadienyl, no examples of insertion of fluorinated olefins into the metal-carbon bond were found. Instead, the alpha-CF₂ group of the perfluorobenzyl ligand in rhodium and iridium complexes is remarkably sensitive to hydrolysis, undergoing reaction with even the smallest traces of water on the surface of glass to give an acarbonyl group. This is a reaction of some significance, as it requires hot concentrated H₂SO₄ to accomplish in the absence of the transition metal. A key intermediate has been isolated in which a water molecule and a perfluorobenzyl group are both bound to a cationic rhodium center. The hydrolysis mechanisms has been studied in detail. The basic findings are that the acidity of the water molecule is strongly enhanced by coordination to rhodium, and that the acidity is strongly dependent on the H-bonding ability of the counterion. This work has been extended to include the first example of hydrolysis of a saturated CF₂ group in a perfluoropropyl ligand.

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FINAL TECHNICAL REPORT

FOR SEPTEMBER 1, 1993 - DECEMBER 31, 1996

AASERT Grant F49620-93-1-0541

NEW ROUTES TO FLUORINATED LIGANDS AND POLYMERS

Principal Investigator:

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

Student Supported: Danielle C. Lindner (formerly Prognos). A U.S. citizen.

Danielle Lindner made excellent progress on the project during this period of the grant.

She satisfied all of Dartmouth College's requirements for the Ph. D. degree, and obtained her Ph. D. degree in January 1997. Her thesis title was "Synthesis and Reactivity of Perfluorobenzyl Complexes of the Group 9 Metals (Co, Rh, Ir)".

She is currently a Postdoctoral Research Associate in the laboratory of Professor Klaus Theopold, at the University of Delaware.

Dr. Lindner prepared the first examples of perfluorobenzyl complexes of the transition metals, and demonstrated that the bond from the perfluorobenzyl ligand to cobalt, rhodium, and iridium is unusually weak. Several complexes were characterized by X-ray crystallography as part of our

continuing collaboration with Professor Arnold Rheingold at the University of Delaware. The α -CF₂ group in several cobalt complexes was shown to be unusually reactive towards coupling with ancillary ligands like cyclopentadienyl, but no examples of insertion of fluorinated olefins into the metal-carbon bond were found, even after exhaustive attempts. Instead, the α -CF₂ group of the perfluorobenzyl ligand in rhodium and iridium complexes is remarkably sensitive to hydrolysis; undergoing reaction with even the smallest traces of water on the surface of glass to give a carbonyl group. This is a reaction of some significance, as it requires hot concentrated H₂SO₄ to accomplish in the absence of the transition metal. Dr. Lindner isolated a key intermediate in this reaction in which a water molecule and a perfluorobenzyl group are both bound to a cationic rhodium center, and has studied the hydrolysis mechanism in detail. The basic findings are that the acidity of the water molecule is strongly enhanced by coordination to rhodium, and that the acidity is strongly dependent on the H-bonding ability of the counterion. Danielle also extended this work to include the first example of hydrolysis of a saturated CF₂ group in a perfluoropropyl ligand.

In addition to the two papers already published, three more are in preparation.

Papers Acknowledging AFOSR Support under this grant:

1. R. P. Hughes, D. C. Lindner, A. L. Rheingold, and G. P. A. Yap
Perfluorobenzyl Complexes of Cobalt and Rhodium.
Unusual Coupling Between Pentafluorophenyl and Pentamethylcyclopentadienyl Rings.
Organometallics, 1996, 15, 5678.
2. R. P. Hughes, D. C. Lindner, A. L. Rheingold, and G. P. A. Yap
Synthesis and Structure of the Thallium(I) Salt of the
[Tetrakis{3,5-bis(trifluoromethyl)phenyl}borate] Anion
Inorg. Chem., 1997, in the press.