

Direct cupration of fluoroform:

A novel and economical route to CuCF_3
for a variety of trifluoromethylation
reactions

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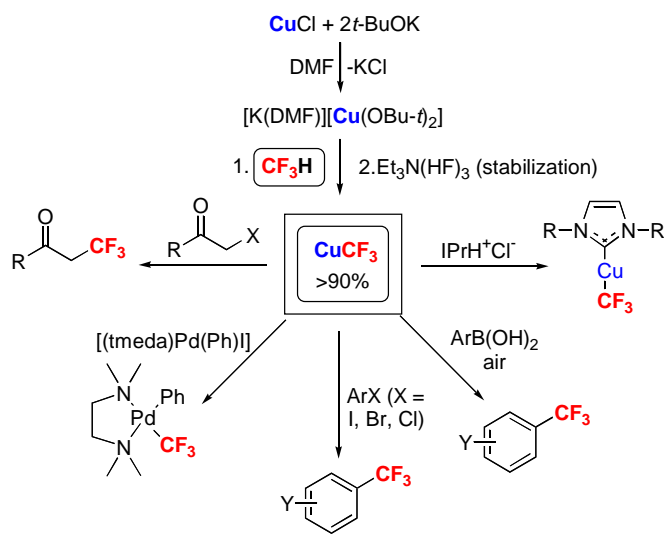
Direct cupration of fluoroform: A novel and economical route to CuCF_3 for a variety of trifluoromethylation reactions

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Trifluoromethylated building blocks and intermediates are in exceptionally high demand for the synthesis of agrochemicals, pharmaceuticals, and specialty materials. Readily available fluoroform, CHF_3 , a side-product of Teflon manufacturing, would be by far the best CF_3 source for various trifluoromethylation reactions.¹ Chemoselective activation of fluoroform, however, is highly challenging.

We have recently discovered the first reaction of direct cupration of fluoroform² and established its mechanism.³ Treatment of CuCl reacts with 2 equiv of $t\text{-BuOM}$ ($M = \text{K}, \text{Na}$) in DMF produces novel dialkoxycuprates $[\text{M}(\text{DMF})_n]^+[\text{Cu}(\text{O}Bu\text{-}t)_2]^-$ (X-ray) that readily metalate CHF_3 at room temperature and atmospheric pressure.² The resultant CuCF_3 (>90% yield) has been successfully used for highly efficient, low-cost trifluoromethylation reactions of a variety of organic and inorganic substrates.^{2,4-7}



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- (2) Zanardi, A.; Novikov, M. A.; Martin, E.; Benet-Buchholz, J.; Grushin, V. V. *J. Am. Chem. Soc.* **2011**, *133*, 20901.
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- (4) Novák, P.; Lishchynskiy, A.; Grushin, V. V. *Angew. Chem. Int. Ed.* **2012**, *51*, 7767.
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- (6) Lishchynskiy, A.; Novikov, M. A.; Martin, E.; Escudero-Adán, E. C.; Novák, P.; Grushin, V. V. *J. Org. Chem.* **2013**, *78*, DOI:10.1021/jo401423h.
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Vladimir Grushin, a native of Moscow, Russia, obtained his PhD degree from Moscow State University (1984). He then spent several years doing research at the Institute of Organo-Element Compounds of the Russian Academy of Sciences and at the University of Ottawa before joining the faculty at Wilfrid Laurier University, Ontario, Canada. In 1997, he took a research position at DuPont CR&D in Wilmington, Delaware. After 12 years with DuPont, he returned to academia in 2010 with an appointment as Senior Group Leader at the Institute of Chemical Research of Catalonia (ICIQ) in Tarragona, Spain. His research interests span organic and inorganic chemistry, including catalysis and organometallic fluorine chemistry.

EDUCATION

Moscow State University, Moscow, Russia, Ph.D. (Organometallic-Organic Chemistry), 1984; Thesis Advisor: Dr. T. P. Tolstaya
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PROFESSIONAL EXPERIENCE

Senior Group Leader, Institut Català d'Investigació Química (ICIQ), Spain, 2010 - now

Principal Investigator, DuPont Central Research & Development, Wilmington, Delaware, U.S.A. 1997 - 2009
Adjunct Prof., Guelph-Waterloo Center for Graduate Research in Chemistry, University of Waterloo, Waterloo, Ontario, Canada 1996 - 1997
Asst. Prof., Wilfrid Laurier University, Waterloo, Ontario, Canada, 1995 - 1997
Research Associate, Dept. of Chemistry, University of Ottawa, Ottawa, Ontario, Canada, 1989 - 1995
Senior Research Scientist, Research Scientist, Junior Research Scientist, Institute of Organo-Element Compounds (INEOS) of the U.S.S.R. Academy of Sciences, Moscow, Russia, 1979 - 1989

AWARDS & HONORS

JSPS Senior Fellowship, Japan Society for the Promotion of Science, 2012
Syngenta Lectureship, 2011
DuPont Senior Vice President Patent Award and Plaque, 2007
DuPont Crop Protection – DuPont CR&D Award for Innovation in Research, 2007
DuPont Senior Vice President Patent Award and Plaque 2006
DuPont New Faculty Grant, 1996