Journal of Fluorine Chemistry 131 (2010) 1049–1056

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Graphical Abstracts/J. Fluorine Chem. 131 (2010) 1049–1056

J. Fluorine Chem., 131 (2010) 1059

Fluorine as a ligand substituent in organometallic chemistry: A second chance and a second research career

Russell P. Hughes

Chemistry Department, Dartmouth College, 6128 Burke Laboratory, Hanover, NH 03755-3564, USA

An historical overview of some of the author's contributions to the organometallic chemistry of fluorinated organic ligands is presented.

M—C—H vs M—C—F

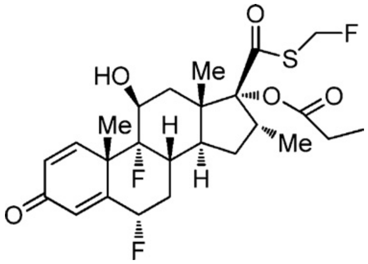
J. Fluorine Chem., 131 (2010) 1071

Fluorine in health care: Organofluorine containing blockbuster drugs

David O'Hagan

School of Chemistry and Centre for Biomolecular Sciences, University of St Andrews, St Andrews KY16 9ST, UK

Organofluorine compounds have had a significant impact in the development of pharmaceutical products. The structures, modes of action and synthesis of the leading blockbuster pharmaceuticals of this class are highlighted. Currently 30% of the top thirty drugs by sales contain a fluorine atom.



J. Fluorine Chem., 131 (2010) 1082

Preparation of *E*-(1,2-difluoro-1,2-ethenediyl)bis(tributylstannane)

Qibo Liu, Donald J. Burton

Department of Chemistry, University of Iowa, IA 52242, USA

Chlorotrifluoroethene is converted in situ to [$F_2C{=}CFSiMe_3$]. The crude [$F_2C{=}CFSiMe_3$] solution is reduced with lithium aluminum hydride to ($HFC{=}CFSiMe_3$), which (without isolation) is converted to (Z)-$HFC{=}CFSnBu_3$. Subsequent metallation and trapping of the vinyllithium reagent with Bu_3SnCl gives (*E*)-$Bu_3SnCF{=}CFSnBu_3$ in 73% overall yield. Only two isolation steps are required and the use of Me_3SiCl and $F_2C{=}CFCl$ provides a cheap, economical route to this useful synthon.

$$F_2C{=}CFCl \dashrightarrow [F_2C{=}CFSiMe_3] \dashrightarrow (Z)\text{-}[HFC{=}CFSiMe_3]$$

$$\dashrightarrow (Z)\text{-}[HFC{=}CFSnBu_3] \dashrightarrow (E)\text{-}Bu_3SnCF{=}CFSnBu_3$$

doi:10.1016/S0022-1139(10)00248-4

J. Fluorine Chem., 131 (2010) 1086

Synthesis of tetrahydropyrido- and pyrido-[1′,2′:1,2]imidazo[4,5-*b*]pyrazine derivatives

Emma L. Parks[a], Graham Sandford[a], Dmitrii S. Yufit[a,b], Judith A.K. Howard[a,b], John A. Christopher[c], David D. Miller[c]

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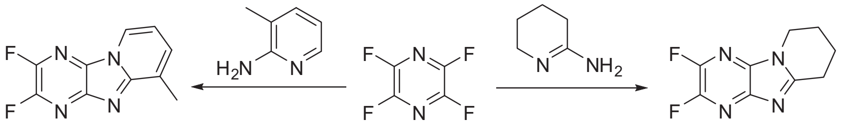
[b]*Chemical Crystallography Group, Department of Chemistry, Durham University, South Road, Durham DH1 3LE, UK*
[c]*GlaxoSmithKline R&D, Medicines Research Centre, Gunnels Wood Road, Stevenage, Hertfordshire SG1 2NY, UK*

Reactions of tetrafluoropyridazine with iminopiperidine and 2-aminopiccoline gave novel tetrahydropyrido- and pyrido-[1′,2′:1,2]imidazo[4,5-*b*]pyrazine heterocyclic frameworks respectively in high yields.

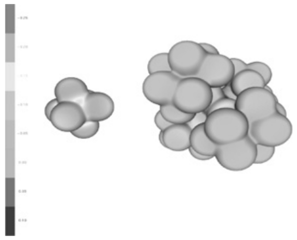


J. Fluorine Chem., 131 (2010) 1091

Anodic oxidation of organometallic sandwich complexes using $[Al(OC(CF_3)_3)_4]^-$ or $[AsF_6]^-$ as the supporting electrolyte anion

Michael P. Stewart[a], Lacey Marina Paradee[a], Ines Raabe[b], Nils Trapp[b], John S. Slattery[b], Ingo Krossing[b], William E. Geiger[a]

[a]*Department of Chemistry, University of Vermont, Burlington, VT 05405, USA*
[b]*Institut für Anorganische und Analytische Chemie and Freiburger Materialforschungszentrum FMF, Albert-Ludwigs-Universität Freiburg, Albertstr. 21, 79104 Freiburg, Germany*



The anodic electrochemical behavior of several monometallic and dimetallic sandwich complexes was studied in dichloromethane containing either $[Al(OC(CF_3)_3)_4]^-$ or $[AsF_6]^-$ as the supporting electrolyte anion. The former behaves as a weakly-coordinating, non-nucleophilic anion towards reactive organometallic cation radicals, whereas the latter behaves more like a traditional small anion.

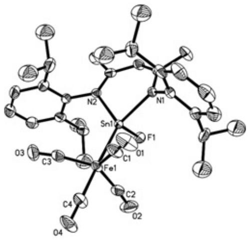
J. Fluorine Chem., 131 (2010) 1096

Preparation of iron carbonyl complexes of germanium(II) and tin(II) each with a terminal fluorine atom

Anukul Jana[a], Prinson P. Samuel[a], Herbert W. Roesky[a], Carola Schulzke[b]

[a]*Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, 37077 Göttingen, Germany*
[b]*School of Chemistry, Trinity College Dublin, Dublin 2, Ireland*

The iron carbonyl complexes of germanium(II) fluoride and tin(II) fluoride have been prepared from the corresponding fluoride by the reaction with diiron nonacarbonyl.



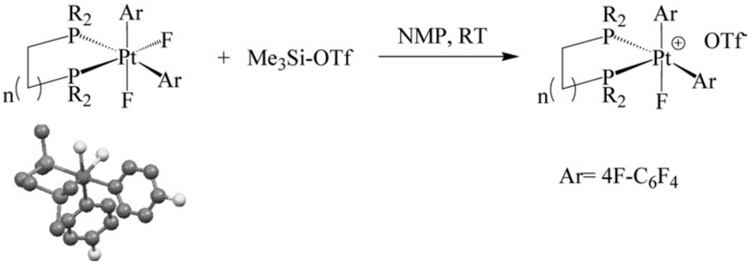
J. Fluorine Chem., 131 (2010) 1100

Synthesis and reactivity of unsymmetrical difluoro Pt(IV) complexes

Anette Yahav-Levi, Israel Goldberg, Arkadi Vigalok

School of Chemistry, The Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, Tel Aviv 69978, Israel

Difluoro Pt(IV) complexes $(P–P)Pt(Ar)_2F_2$ were prepared and characterized. One of the fluoro ligands can be selectively removed from the Pt coordination sphere giving the cationic product with the phosphine ligand trans to the empty coordination site.



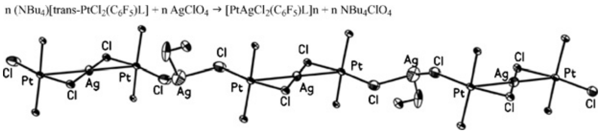
J. Fluorine Chem., 131 (2010) 1103

A new class of polymeric complexes having Pt–Ag interactions: Crystal structure of $|\{[(PPh_3)\,(C_6F_5)Pt(\mu\text{-}Cl)]_2Ag\}(\mu\text{-}Cl)_2Ag(MeOH)|_n$

Irene Ara, Javier Aranaz, Juan Forniés

Departamento de Química Inorgánica and Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, E-50009 Zaragoza, Spain

The reaction of $(NBu_4)[\textit{trans}\text{-}PtCl_2(C_6F_5)L]$ (L = PPh_3, $AsPh_3$) with $AgClO_4$ (1:1) ratio leads to the polymeric complexes $[PtAgCl_2(C_6F_5)L]_x$ (L = PPh_3, $AsPh_3$). The structure of complex $|\{[(PPh_3)(C_6F_5)Pt(\mu\text{-}Cl)]_2Ag\}(\mu\text{-}Cl)_2$ Ag $(MeOH)|_n$ is a chain polymer in which the silver atoms are in two different environments with or without Pt–Ag bond.



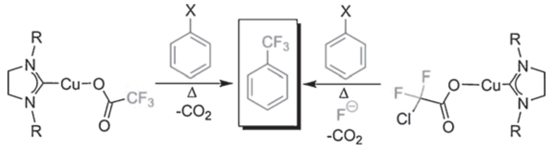
J. Fluorine Chem., 131 (2010) 1108

Decarboxylative trifluoromethylation of aryl halides using well-defined copper–trifluoroacetate and –chlorodifluoroacetate precursors

Kristen A. McReynolds[a], Robert S. Lewis[a], Laura K.G. Ackerman[a], Galyna G. Dubinina[a], William W. Brennessel[b], David A. Vicic[a]

[a]*Department of Chemistry, University of Hawaii, 2545 McCarthy Mall, Honolulu, HI 96822, United States*
[b]*The X-ray Crystallographic Facility, Department of Chemistry, University of Rochester, Rochester, NY 14627, United States*

New synthetic routes to (NHC)copper–trifluoroacetate and –chlorodifluoroacetate complexes were developed (NHC = *N*-heterocyclic carbenes) so baseline reactivity patterns could be established for the decarboxylative trifluoromethylation of organic halides. In the presence of aryl halides, loss of CO_2 from these new precursors occurred at 160 °C concurrent with the formation of aryl–CF_3.

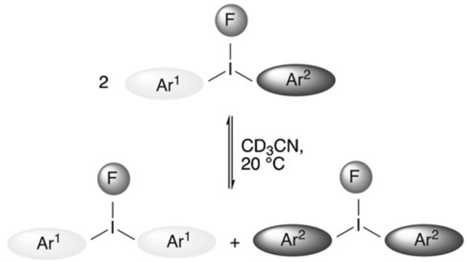


J. Fluorine Chem., 131 (2010) 1113

Fluoride-promoted ligand exchange in diaryliodonium salts

Bijia Wang, Ronald L. Cerny, ShriHarsha Uppaluri, Jayson J. Kempinger, Stephen G. DiMagno

Department of Chemistry and Nebraska Center for Materials and Nanoscience, University of Nebraska-Lincoln, Lincoln, NE 68588-0304, USA



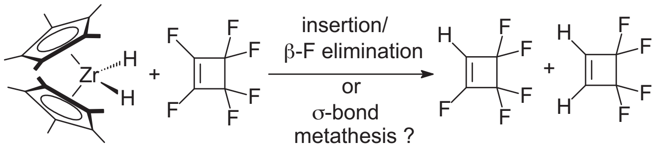
J. Fluorine Chem., 131 (2010) 1122

Mechanistic investigation of vinylic carbon–fluorine bond activation of perfluorinated cycloalkenes using $Cp^*{}_2ZrH_2$ and $Cp^*{}_2ZrHF$

Bradley M. Kraft[a], Eric Clot[b], Odile Eisenstein[b], William W. Brennessel[c], William D. Jones[c]

[a]*St. John Fisher College, 3690 East Avenue, Rochester, NY 14618, United States*
[b]*Institut Charles Gerhardt, Université Montpellier 2, CNRS 5253, Case Courrier 1501, Place E. Bataillon, 34095 Montpellier, France*
[c]*Department of Chemistry, University of Rochester, Rochester, NY 14627, United States*

$Cp^*{}_2ZrH_2$ reduces perfluorocycloolefins by a sigma-bond metathesis pathway.



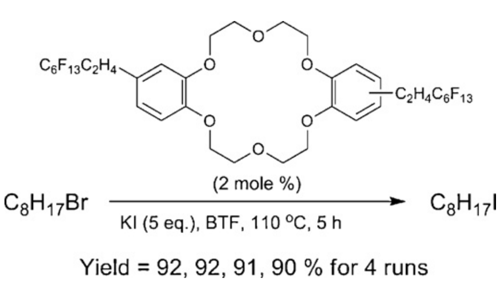
J. Fluorine Chem., 131 (2010) 1133

Di(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-dibenzo-18-crown-6: A "light fluorous" recyclable phase transfer catalyst

Benoit Gourdet, Kuldip Singh, Alison M. Stuart, José A. Vidal

Department of Chemistry, University of Leicester, Leicester LE1 7RH, UK

The "light fluorous" crown ether can be recycled efficiently by fluorous solid-phase extraction and it gives better PTC catalytic activity than dibenzo-18-crown-6 in aliphatic and aromatic nucleophilic substitutions.

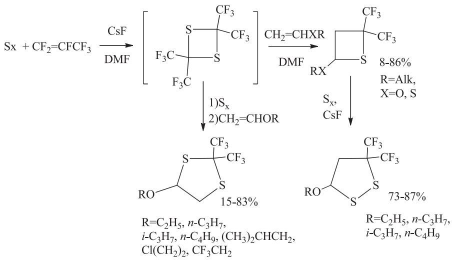


J. Fluorine Chem., 131 (2010) 1144

Remarkable effect of metal fluoride catalyst on reaction of hexafluoropropene, sulfur and vinyl ethers. Convenient synthesis of 2,2-bis(trifluoromethyl)-4-R-thietanes, 3,3-bis(trifluoromethyl)-5-R-1,2-dithiolanes and 2,2-bis(trifluoromethyl)-4-R-1,3-dithiolanes

Viacheslav A. Petrov[a], Will Marshall[b]

DuPont CR&D, Experimental Station, PO Box 80500, Wilmington, DE 19880-0500, United States
DuPont Corporate Center for Analytical Sciences, Experimental Station, PO Box 80500, Wilmington, DE 19880-0500, United States



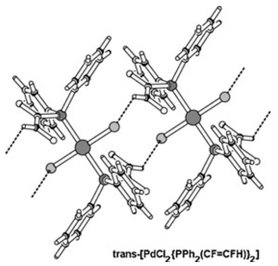
J. Fluorine Chem., 131 (2010) 1156

The synthesis and single-crystal X-ray structures of palladium(II) and platinum(II) complexes of the difluorovinyl and 1-chloro-2-fluorovinyl-substituted phosphines, PPh_2(Z-CF═CFH) and PPh_2(E-CCl═CFH)

Nicholas A. Barnes, Alan K. Brisdon, Cheryl Fish, James V. Morey, Robin G. Pritchard, John E. Warren

School of Chemistry, The University of Manchester, Oxford Rd, Manchester, M13 9PL, UK

The synthesis of a series of Pd(II) and Pt(II) complexes of partially fluorinated ligands of the type $Ph_2P(CX{=}CFH)$ (X = F, Cl) are reported. A comparison of the steric, electronic and solid-state structural mofits of these ligands and complexes with previously reported analogues is made.


$trans$-[$PdCl_2\{PPh_2(CF{=}CFH)\}_2$]

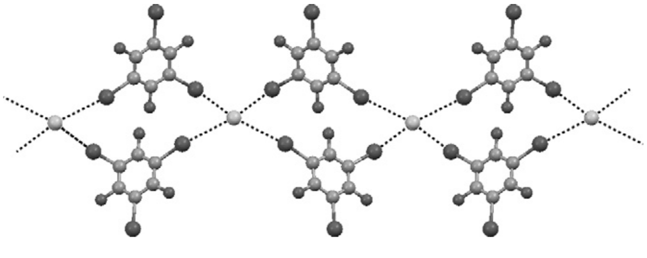
J. Fluorine Chem., 131 (2010) 1165

Halide anion-templated assembly of di- and triiodoperfluorobenzenes into 2D and 3D supramolecular networks

Gabriella Cavallo[a], Serena Biella[a,b], Jian Lü[a], Pierangelo Metrangolo[a,b], Tullio Pilati[c], Giuseppe Resnati[a,b,c], Giancarlo Terraneo[a,b]

[a]*NFMLab - D.C.M.I.C. "Giulio Natta", Politecnico di Milano, Via L. Mancinelli 7, 20131 Milan, Italy*
[b]*CNST - IIT@POLIMI, Politecnico di Milano, Via G. Pascoli 70/3, 20133 Milan, Italy*
[c]*C.N.R. - I.S.T.M., University of Milan, Via C. Golgi 19, 20133 Milan, Italy*

Supramolecular networks formed by halide anions and di- and triiodoperfluorobenzenes.



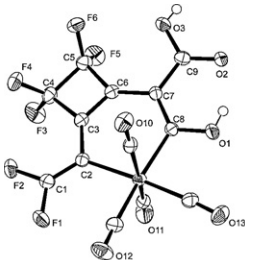
J. Fluorine Chem., 131 (2010) 1173

Fluorinated butatrienes

Christian Ehm, Floris A. Akkerman, Dieter Lentz

Institut für Chemie und Biochemie, Abt. Anorganische Chemie, Freie Universität Berlin, Fabeckstraße 34-36, 14195 Berlin, Germany

Major improvements in the synthesis of 1,1,4,4-tetrafluorobutatriene and first attempts to synthesize 1,1-difluorobutatriene are presented. A partially hydrolyzed iron complex containing two former tetrafluorobutatriene units and an inserted CO unit could be isolated and characterized by X-ray crystallography.



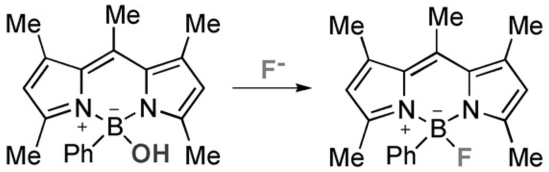
J. Fluorine Chem., 131 (2010) 1182

Substitution of hydroxide by fluoride at the boron center of a BODIPY dye

Todd W. Hudnall, Tzu-Pin Lin, François P. Gabbaï

Department of Chemistry, Texas A&M University, College Station, TX 77843, United States

4-Hydroxo-4-phenyl-1,3,5,7,8-pentamethyl-3a,4a-diaza-4-bora-s-indacene reacts with fluoride anions under acidic conditions to afford the corresponding fluoride derivative 4-fluoro-4-phenyl-1,3,5,7,8-pentamethyl-3a,4a-diaza-4-bora-s-indacene.



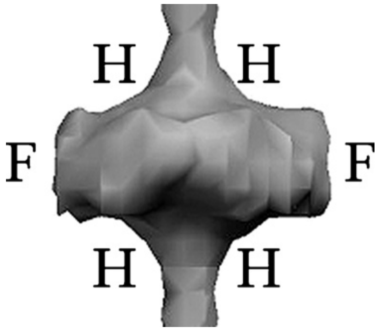
J. Fluorine Chem., 131 (2010) 1187

The effect of trifluoromethyl groups in the para positions of a perfluoroaryl phosphine: A comparison of the structures of $[\{\eta^5,\kappa P\text{-}C_5Me_4CH_2C_6F_3X\text{-}5\text{-}P(C_6F_4X\text{-}4)\text{-}2\text{-}CH_2P(C_6F_4X\text{-}4)_2\}RhCl_2]$, X = F and CF_3

Graham C. Saunders

Department of Chemistry, The University of Waikato, Hamilton, New Zealand

Replacement of the para fluorine atoms of $\{(C_6F_5)_2P\}_2CH_2$ has a minimal steric or electronic effect on the title complex, but dramatically affects the packing in the crystal structure generating channels of large fluoroaryl cavities separated by aliphatic constrictions.

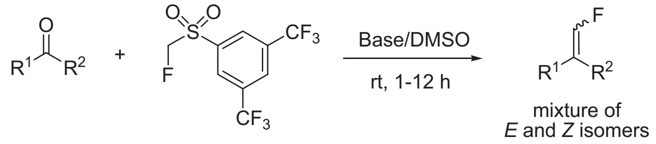


J. Fluorine Chem., 131 (2010) 1192

Synthesis of monofluoroalkenes via Julia–Kocienski reaction

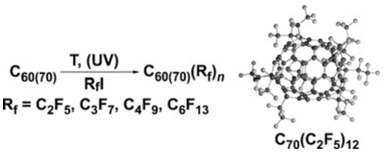
G.K. Surya Prakash, Anton Shakhmin, Mikhail Zibinsky, Istvan Ledneczki, Sujith Chacko, George A. Olah

Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, 837 Bloom Walk, Los Angeles, CA 90089-1661, USA



J. Fluorine Chem., 131 (2010) 1198

High-temperature and photochemical syntheses of C_{60} and C_{70} fullerene derivatives with linear perfluoroalkyl chains



Natalia B. Shustova[a], Ivan E. Kareev[b,c], Igor V. Kuvychko[a], James B. Whitaker[a], Sergey F. Lebedkin[c], Alexey A. Popov[d], Lothar Dunsch[d], Yu-Sheng Chen[e], Konrad Seppelt[f], Steven H. Strauss[a], Olga V. Boltalina[a]
[a]*Department of Chemistry, Colorado State University, Fort Collins, CO 80523, USA*
[b]*Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka 142432, Russia*
[c]*Forschungszentrum Karlsruhe, Institute for Nanotechnology, Karlsruhe 76021, Germany*
[d]*Department of Electrochemistry and Conducting Polymers, Leibniz Institute for Solid State and Materials Research, 01069 Dresden, Germany*
[e]*ChemMatCARS, University of Chicago Advanced Photon Source, Argonne, IL 60439, USA*
[f]*Institut für Anorganische und Analytische Chemie, Freie Universität Berlin, 14195 Berlin, Germany*
[e]*ChemMatCARS, University of Chicago Advanced Photon Source, Argonne, IL 60439, USA*
[f]*Institut für Anorganische und Analytische Chemie, Freie Universität Berlin, 14195 Berlin, Germany*

New fullerene $(R_f)_n$ compounds were prepared in high-temperature reactions, and characterized by spectroscopic, electrochemical and structural methods.

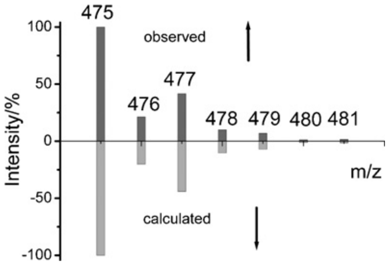
J. Fluorine Chem., 131 (2010) 1213

Liquid injection field desorption/ionization of transition metal fluoride complexes

Trevor A. Dransfield, Ruqia Nazir, Robin N. Perutz, Adrian C. Whitwood

Department of Chemistry, University of York, York YO10 5DD, UK

Metal fluoride complexes of nickel, rhodium, ruthenium, titanium and zirconium have been characterized by liquid injection field desorption/ionization (LIFDI) mass spectrometry. Most show the molecular ion as base peak. Commoner ionization methods give very poor results by comparison.



J. Fluorine Chem., 131 (2010) 1218

Halogen-bonded and interpenetrated networks through the self-assembly of diiodoperfluoroarene and tetrapyridyl tectons

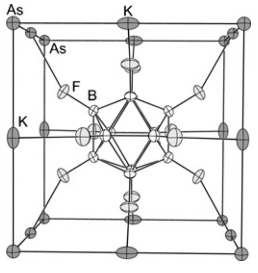
Michele Baldrighi[a], Pierangelo Metrangolo[a,b], Franck Meyer[a], Tullio Pilati[c], Davide Proserpio[d], Giuseppe Resnati[a,b,c], Giancarlo Terraneo[a,b]

[a]*NFMLab - D.C.M.I.C. “Giulio Natta”, Politecnico di Milano, Via L. Mancinelli 7, 20131 Milan, Italy*
[b]*CNST - IIT@POLIMI, Politecnico di Milano, Via G. Pascoli 70/3, 20133 Milan, Italy*
[c]*C.N.R. - I.S.T.M., University of Milan, Via C. Golgi 19, 20133 Milan, Italy*
[d]*Department of Structural Chemistry and Inorganic Stereochemistry, University of Milan, 21, via Venezian, 20133 Milan, Italy*

Expansion strategy design of interpenetrated networks with diiodoperfluoroarenes.

J. Fluorine Chem., 131 (2010) 1225

Co-crystallization of octahedral and icosahedral fluoroanions in $K_3(AsF_6)(B_{12}F_{12})$ and $Cs_3(AsF_6)(B_{12}F_{12})$. Rare examples of salts containing fluoroanions with different shapes and charges



Dmitry V. Peryshkov[a], Evgeny Goreshnik[b], Zoran Mazej[b], Steven H. Strauss[a]

[a]*Department of Chemistry, Colorado State University, Fort Collins, CO 80523, USA*
[b]*Jožef Stefan Institute, 1000 Ljubljana, Slovenia*

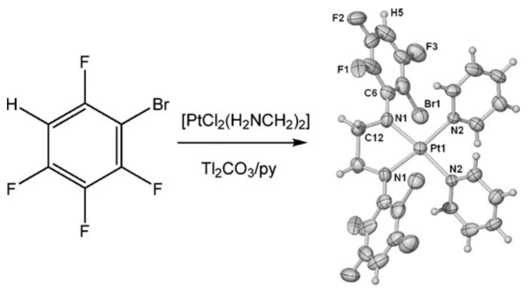
Combining (K,Cs)AsF_6 and $Cs_2B_{12}F_{12}$ in HF produced crystals that are shown by Raman spectroscopy and X-ray diffraction to be $K_3(AsF_6)(B_{12}F_{12})$ or $Cs_3(AsF_6)(B_{12}F_{12})$, which exhibit a modified anti-perovskite structure and are rare examples of crystals that simultaneously contain octahedral and icosahedral species and contain fluoroanions with different shapes and charges.

J. Fluorine Chem., 131 (2010) 1229

Syntheses and structures of N-polyfluorophenyl- and *N*,*N*′-bis (polyfluorophenyl)ethane-1,2-diaminato (1- or 2-) platinum(II) complexes

Andrew R. Battle[a], Alan M. Bond[b], Alex Chow[b], Daisy P. Daniels[b], Glen B. Deacon[b], Trevor W. Hambley[a], Peter C. Junk[b], Dayna N. Mason[b], Jun Wang[b]

[a]*School of Chemistry, University of Sydney, NSW 2006, Australia*
[b]*School of Chemistry, Monash University, Clayton, VIC 3800, Australia*



Reactions of Tl_2CO_3 and ethylenediamineplatinum(II) complexes give a variety of N-polyfluorophenyl- or *N*,*N*′-bis(polyfluorophenyl)ethane-1,2-diaminato (1- or 2-) platinum (II) complexes.

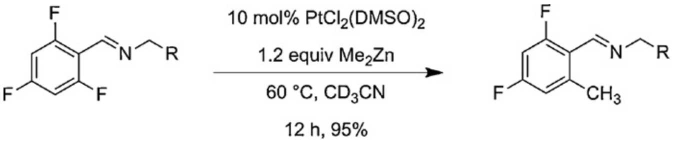
J. Fluorine Chem., 131 (2010) 1237

Pt(II)Cl_2(DMSO)$_2$-catalyzed cross-coupling of polyfluoroaryl imines

Alex D. Sun, Jennifer A. Love

Department of Chemistry, 2036 Main Mall, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z1

$PtCl_2(DMSO)_2$ has been identified as a readily accessible and effective C–F activation precatalyst. We report herein the study of reaction optimization and substrate scope. A comparison is made with previously reported $[Pt_2Me_4(SMe_2)_2]$ and $PtCl_2(SMe_2)_2$ precatalysts.

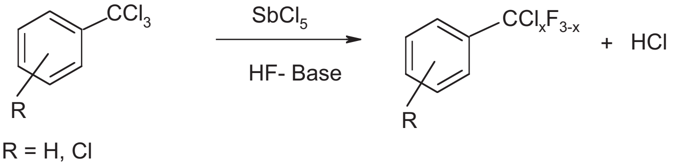


J. Fluorine Chem., 131 (2010) 1241

Selective fluorination of substituted trichloromethyl benzenes by HF in liquid phase: Preparation of fluorinated building blocks

Alexandre Piou, Stephane Celerier, Sylvette Brunet

Laboratoire de Catalyse en Chimie Organique, UMR CNRS 6503, Université de Poitiers, Faculté des Sciences Fondamentales et Appliquées 40, Avenue du Recteur Pineau, 86022 Poitiers cedex, France



The selective fluorination by successive Cl/F exchanges of α,α,α-trichlorotoluenes was studied. Depending on the fluorinating system, it could be possible to adapt the operating conditions in order to prepare selectively the mono, di or trichlorinated compound with a good conversion of the starting chlorinated compounds.

J. Fluorine Chem., 131 (2010) 1247

Structure and reactivity of a planar chiral naphthylferrocenylcopper heteroaggregate

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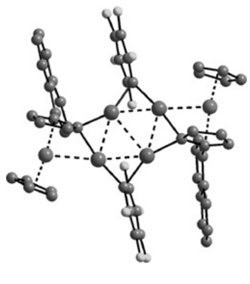

A chiral 2-naphthylferrocenylcopper heteroaggregate was prepared in high yield by reaction of (S_p-2-naphthylferrocenyl)trimethyltin with $(C_6F_5Cu)_4$ and its reactivity toward boron halides was examined.

J. Fluorine Chem., 131 (2010) 1252

$K_2B_{12}F_{12}$: A rare A_2X structure for an ionic compound at ambient conditions

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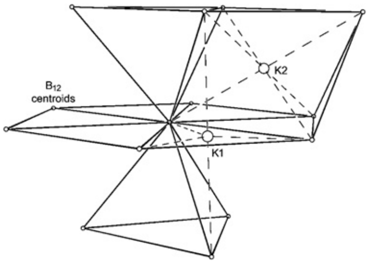
The structure of the $K_2B_{12}F_{12}$, crystallized from an aqueous solution, is extremely rare for an A_2X salt. It consists of an expanded HCP array of $B_{12}F_{12}^{2-}$ anion centroids with half of the K^+ ions filling O_h holes and half filling D_{3h} trigonal holes midway between two "empty" T_d holes.



J. Fluorine Chem., 131 (2010) 1257

A terminal palladium fluoride complex supported by an anionic PNP pincer ligand

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A terminal palladium fluoride supported by an ^{F}PNP ligand has been synthesized and characterized. This complex possesses an approximately square–planar environment about Pd and a short Pd–F bond. It reacts with silane reagents containing electron-with drawing groups by exchange of fluorine with a substituent on silicon.