Dalton Transactions

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Approaches to Prepare Perfluoroalkyl and Pentafluorophenyl Copper Couples for Cross-Coupling Reactions with Organohalogen Compounds

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Synthesis of perfluoroorgano copper lithium and silver couples

$$2\,R_f I \;+\; 2\,n\text{-}C_4H_9Li \xrightarrow[-\,2\,n\text{-}C_4H_9I]{} 2LiR_f \xrightarrow[-\,LiBr]{+\,CuBr} Li(R_f)_2Cu$$

$$2\;AgR_f \;+\; Cu \longrightarrow Cu(R_f)_2Ag \;+\; Ag$$

Journal Name

ARTICLE

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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The reactions of iodoperfluoroalkanes $C_nF_{2n+1}I$ (n = 2, 3, 4) and n-BuLi at low temperature give NMR spectroscopic evidence for LiC_nF_{2n+1} which were converted into $LiCu(C_nF_{2n+1})_2$ derivatives upon treatment by 0.5 mol copper (I) bromide, CuBr. An alternative route to obtain perfluoroorgano copper couples, $Cu(R_f)_2Ag$ (R_f = n-C_3F_7, n-C_4F_9, C_6F_5) was opened from reactions of the corresponding perfluoroorgano silver(I) reagents, AgR_f, and elemental copper through redox transmetallations. The composition of the resulting reactive intermediates was investigated by means of ^{19}F NMR spectroscopy and ESI mass spectrometry. Perfluoro-n-propyl and perfluoro-n-butyl copper-silver reagents prepared by the oxidative transmetallation route exhibited good properties in C-C bond formation reactions with acid chlorides even under moderate conditions. Substitution of bromine directly bounded to aromatics for perfluoroalkyl groups was achieved at elevated temperature, while success in halide substitution reactions using lithium copper couples remained poor.

Introduction

Diorgano lithium copper couples, generally written as LiR_2Cu, have been attracting remarkable attention as effective and selective reagents for substitution of halogens by functional groups in a variety of different substrates and have even been used effectively in stereospecific synthesis.[1]

Ethereal solutions of non-fluorine containing lithium diorganocuprates are conveniently prepared at 0 °C in an inert atmosphere via reactions of alkyllithium compounds and copper iodide or bromide in molar ratios of 2:1; mixed lithium diorganocuprates can be obtained by the reaction of monoorganocopper reagent with organolithium species (Scheme 1).

A mixed fluorine containing lithium diorganocuprate $Li(CH_3)(C_6F_5)Cu$ – the only example of such a species to our knowledge mentioned so far – was formulated in the reaction of methylcopper and pentafluorophenyllithium in diethyl ether at -70 °C and was used in the reaction with benzoyl chloride at ambient temperature. After routine work-up procedures, acetophenone (34%) and 2,3,4,5,6-pentafluorobenzophenone (80%) were obtained.[2]

$$2RLi + CuX \longrightarrow LiR_2Cu + LiX$$

$$X = Br, I$$

$$R'Li + RCu \longrightarrow Li(R'R)Cu$$

Scheme 1 Lithium and mixed lithium diorganocuprates

Perfluoroorgano copper species CuR_f (R_f = CF_3, C_2F_5, n-C_3F_7, n-C_4F_9, C_6F_5) have been prepared by several methods.[3-6] Mainly perfluoroorgano zinc and cadmium were used to prepare the corresponding copper reagents via halide exchange reactions (Scheme 2).[3a]

However, all reactions described so far did neither clearly point out the formation of bis(perfluoroorgano)cuprates, $[Cu(R_f)_2]^-$ nor halogenocuprates $[Cu(R_f)X]^-$, although these derivatives exhibit to be the reactive intermediates in nucleophilic substitution.[3b] On the basis of these results, equilibria may be suggested as outlined below (Scheme 3).

The involvement of highly reactive copper(II) and copper(III) in these reaction sequences especially for the higher perfluoroalkyl and the pentafluorophenyl derivative can neither be proved nor excluded[6].

$$MR_fX + CuX' \longrightarrow CuR_f + MXX'$$

$$M = Zn, Cd;\ X = Br, I;\ R_f = CF_3, C_2F_5;\ X' = Br, I$$

Scheme 2 Synthesis of perfluoroalkyl copper compounds from perfluoroorgano zinc and cadmium and copper iodide or bromide

$$MR_fX + CuX' \longrightarrow CuR_f \rightleftharpoons [Cu(R_f)_2]Cu$$

Scheme 3 Equilibria in synthesis of perfluoroalkyl copper compounds

The involvement of reactive copper species formed by the system CuX / KF / Me_3SiR_f in aromatic substitutions is

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† This paper is dedicated to the memory of our colleague Dr Wieland Tyrra (08.03.1961-29.11.2014) who sadly passed away during the preparation of this article.

discussed in the literature[7] without any concrete formulation of the intermediately formed species.

With the synthesis of trifluoromethyl copper compounds via an oxidative route not involving any heavier halides a new route to $CuCF_3$ reagents from elemental copper and $AgCF_3$ starting from commercially available trimethyl(trifluoromethyl)silane, silver (I) fluoride and copper powder were described.[8] Excellent synthetic route based on non halide starting material – CF_3H – is developed and used widely nowadays.[9]

In this work we present investigations of the perfluoroorgano lithium copper and silver couples preparation, comparison of their reactivity with perfluoroorganocopper reagents, CuR_f (R_f = n-C_3F_7, n-C_4F_9, C_6F_5), generated via the corresponding perfluoroorganosilver reagents AgR_f and elemental copper through redox transmetallation.

Results and Discussion

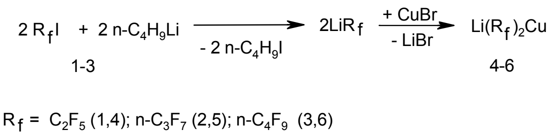
Synthesis of perfluoroorgano copper reagents

Perfluoroorgano lithium copper couples

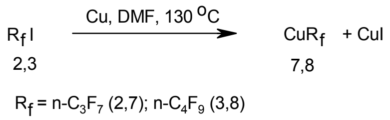
Perfluoroorgano lithium reagents were prepared as intermediates from reactions of pentafluoroiodoethane, C_2F_5I (**1**), n-heptafluoroiodopropane, n-C_3F_7I (**2**) or n-nonafluoroiodobutane, C_4F_9I (**3**) and n-butyllithium in diethylether in a temperature range between –78 °C to –95 °C. Addition of half an equivalent of CuBr at –95 °C (for **1** at –75 °C) and comparison of ^{19}F NMR chemical shifts of n-C_3F_7Li, n-C_4F_9Li, C_3F_7Cu, C_4F_9Cu and copper couples **4-6** (Table 1) gave evidence for the formation of the corresponding perfluoroalkyl lithium copper couples **4-6** in approximately 80% yields (^{19}F NMR) (Scheme 4). In the mixtures of THF and DMF, couples **4-6** are stable up to –10 °C without any observable decomposition (^{19}F NMR data), however, in this temperature range couples **4-6** show only poor reactivity towards halogencontaining aromatic and heterocyclic compounds.

Synthesis of perfluoroalkyl copper compounds from R_fI and elemental copper

Perfluoroalkylcopper derivatives were alternatively prepared from reactions of the corresponding iodoperfluoroalkanes and copper powder in DMF at 130 °C[10] (Scheme 5) for comparative investigation by NMR spectroscopic means.



Scheme 4 Perfluoroorgano lithium copper couples



Scheme 5 Synthesis of perfluoroalkyl copper compounds from R_f I and elemental copper

Perfluoroorgano silver copper couples

On the basis of results achieved with redox transmetallations between $AgCF_3$ and elemental copper,[8a] this work has been extended to investigations involving silver/copper couples, $Ag(R_f)_2Cu$ with R_f being n-C_3F_7, n-C_4F_9 and C_6F_5 (**9-11**). In contrast with longer chain perfluoroalkyls interaction of $AgCF_3$ and elemental copper led to the formation of $CuCF_3$, probably, due to the some specific chemical properties of trifluoromethyl group[8a]. The silver derivatives themselves are conveniently accessible from room temperature reactions of silver(I) fluoride and trimethyl(perfluoroorgano)silanes[11,12] in an appropriate solvent as acetonitrile, propionitrile or DMF (Scheme 6).

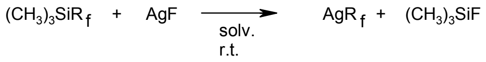
Reactions of AgR_f and elemental copper within reaction times of 30 to 60 minutes gave silver copper couples which were used for further investigations (Scheme 7).

Compounds **9-11** are stable in solution up to approximately 100 °C. Propionitrile, acetonitrile and DMF have been chosen as solvents of choice due to the sufficient solubility of AgF in these media.[12]

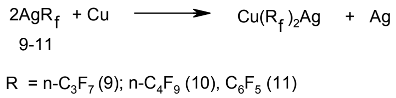
Attempts to use THF as a solvent, gave no evidence for the formation of perfluoroorgano silver copper couples due to a too low solubility of silver fluoride in this medium.

^{19}F NMR spectroscopic (4-11) and mass spectrometric investigations (10-11)

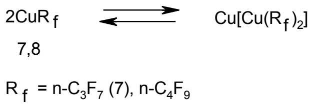
Investigation of solutions of compounds **4-11** by ^{19}F NMR spectroscopy show that a monomeric copper compound $Cu(R_f)$.DMF and an ionic form $Cu[Cu(R_f)_2]$ equilibrate with each other in compounds **7** and **8** (Scheme 8).[4]



Scheme 6 Synthesis of perfluoroalkyl silver compounds from room temperature reactions of silver(I) fluoride and trimethyl(perfluoroorgano)silanes in an appropriate solvent as acetonitrile, propionitrile or DMF



Scheme 7 Preparation of perfluoroorgano silver copper couples



Scheme 8 Equilibrium between monomeric copper compound $Cu(R_f)$.DMF and an ionic form $Cu[Cu(R_f)_2]$

Table 1 Compilation of ^{19}F NMR chemical shifts of perfluoroalkyllithium copper couples, perfluoroalkyl copper compounds, perfluoroalkyl silver copper couples and perfluoroalkyl silver derivatives

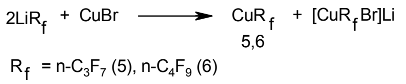
No	Compound	Solvent	T/ °C	δ(α-CF$_2$)	δ(β-CF$_2$)	δ(γ-CF$_2$)	δ(CF$_3$)
4	Li(C$_2$F$_5$)$_2$Cu	Mixture $^{a)}$	-70	-111.8			-82.3
5	Li(n-C$_3$F$_7$)$_2$Cu	Mixture $^{a)}$	-70	-108.5	-122.5		-80.6
6	Li(n-C$_4$F$_9$)$_2$Cu	Mixture $^{b)}$	-70	-108.2	-125.9	-115.3	-81.2
7	Cu(n-C$_3$F$_7$)	DMF	21	-112.4	-125.0		-79.2
	Cu[Cu(n-C$_3$F$_7$)$_2$]	DMF	21	-116.5	-126.5		-81.8
8	Cu(n-C$_4$F$_9$)	DMF	21	-111.1	-123.8	-121.7	-81.0
	Cu[Cu(n-C$_4$F$_9$)$_2$]	DMF	21	-119.0	-126.1	-122.4	-81.6
9	Ag(n-C$_3$F$_7$)$_2$Cu	EtCN	21	-117.1	-126.9		-79.8
	Ag(n-C$_3$F$_7$)$_2$Cu	DMF	21	-118.3	-123.5		-82.6
10	Ag(n-C$_4$F$_9$)$_2$Cu	EtCN	21	-117.2	-125.4	-123.4	-80.9
	Ag(n-C$_4$F$_9$)$_2$Cu	DMF	21	-116.1	-124.8	-122.9	-80.4
	Ag(n-C$_3$F$_7$)	DMF $^{c)}$	-30	-106.5	-123.0		-78.6
	Ag[Ag(n-C$_3$F$_7$)$_2$]	DMF $^{c)}$	-30	-111.5	-124.5		-78.9
	Ag(n-C$_4$F$_9$)	DMF $^{c)}$	-30	-106.8	-125.4	-119.6	-81.2
	Ag[Ag(n-C$_4$F$_9$)$_2$]	DMF $^{c)}$	-30	-112.1	-125.8	-122.2	-81.3
	Li(n-C$_3$F$_7$)	Mixture $^{d)}$	-70	-124.2	-127.2		-78.6
	Li(n-C$_4$F$_9$)	Mixture $^{d)}$	-70	-121.2	-126.5	-122.5	-80.7

a) mixture: Et$_2$O (15 mL)/ n-hexane (5 mL)/ THF (15 mL)/ DMF (15 mL); b) mixture Et$_2$O (10 mL)/ n-hexane (3.6 mL)/ THF (10 mL)/ DMF (10 mL); c) 30% DMF-d$_7$; e) Et$_2$O/ n-hexane.

Chemical shifts of the α-fluorine atom in the ^{19}F NMR spectra of these compounds are in good agreement with those reported for the CF$_2$ groups in the ^{19}F NMR spectra of CuC$_2$F$_5$·DMF (-112.2 ppm) and [Cu(C$_2$F$_5$)$_2$]$^-$ (-116.4 ppm), respectively, indicating similar equilibria as outlined earlier.[13] ^{19}F NMR spectra of compounds **5** and **6** significantly differ from those of compounds **7** and **8** (cf. Table 1) indicating that in these cases the monomeric species CuR$_f$ or presumably adducts with lithium halides formulated as perfluoroalkylhalogeno cuprates, [Cu(R$_f$)X]$^-$ might be dominating (Scheme 9).

Taking into account the influence of the solvent onto chemical shifts as well as considering literature data,[4,13] shifts of α-CF$_2$ groups of CuCF$_2$R$_f$ can be estimated to be –110±3 ppm and those of [Cu(CF$_2$R$_f$)$_2$]$^-$ to be –116±3 ppm. As a consequence of the data surveyed in Table 1, compounds **4-6** may be understood as mainly neutral derivatives, CuCF$_2$R$_f$, or adduct with lithium halides, while **7** and **8** equilibrate in a manner as described in references.[4,13] Compounds **9** and **10** exhibit fluxional character in solution, wherein Ag[Cu(CF$_2$R$_f$)$_2$], Cu[Ag(CF$_2$R$_f$)$_2$], AgCF$_2$R$_f$ and CuCF$_2$R$_f$ exchange with each other (Table 1). Data for the C$_6$F$_5$ derivatives are given in Table 2. Equilibria between CuR$_f$ and LiR$_f$ for compounds **4-6** can nearly be excluded because in the ^{19}F NMR spectra of these compounds signals from Li(R$_f$)$_2$Cu was only observed [for example, chemical shift of α-CF$_2$ group of Li(C$_3$F$_7$)$_2$Cu is -108.5 ppm].

In case of equilibria between CuR$_f$ [chemical shift of α-CF$_2$ group of C$_3$F$_7$Cu is -112.4 ppm] and LiR$_f$ [chemical shift of α-CF$_2$ group of LiC$_3$F$_7$ is -124.2 ppm] one must expect in ^{19}F NMR spectra signals from both of reagents (see Table 1).



Scheme 9 Perfluoroalkylhalogeno cuprates

Table 2 ^{19}F NMR data of AgC$_6$F$_5$,[12] CuC$_6$F$_5$[10] and Ag(C$_6$F$_5$)$_2$Cu (room temperature)

Compound	δ(F-2,6)	δ(F-4)	δ(F-3,5)	Solvent
AgC$_6$F$_5$	-104.7	-157.0	-162.2	EtCN
CuC$_6$F$_5$	-113.4	-164.0	-165.3	CD$_3$CN
Cu(C$_6$F$_5$)$_2$Ag	-111.4	-158.7	-162.6	EtCN

Additionally, the involvement of higher aggregates such as [Cu$_2$(CF$_2$R$_f$)$_3$]$^-$ and related seem to be plausible on the basis of negative ESI mass spectrometric studies of the pentafluorophenyl derivative **11**. Such behaviour is supported by results of A. Sundararaman et al.[14] who intensively studied the structural diversity of CuC$_6$F$_5$ in solution and solid state. ^{19}F NMR data (Table 2) as well as negative ESI mass spectra especially for the pentafluorophenyl derivatives reveal that these silver copper couples are best described as Ag(R$_f$)$_2$Cu.

The perfluoroalkyl reagents are extremely sensitive to moisture and air but cannot be handled for mass spectrometric analyses in an absolute inert atmosphere. As a consequence under the influence of moisture, ions such as [Cu(OCOC$_2$F$_5$)$_2$]$^-$, [Ag(OCOC$_2$F$_5$)$_2$]$^-$, [Cu(C$_3$F$_7$)(OCOC$_2$F$_5$)]$^-$, and [Ag(C$_3$F$_7$)(OCOC$_2$F$_5$)]$^-$ were found as most intensive peaks in the spectra of **9**. Analogous peaks were detected in the mass spectra of **10**. Mass spectra of Cu(C$_6$F$_5$)$_2$Ag exhibit ions of significant intensities for [Ag(C$_6$F$_5$)$_2$]$^-$ as well as [Cu(C$_6$F$_5$)$_2$]$^-$ and higher aggregates [Cu$_m$Ag$_n$(C$_6$F$_5$)$_{m+n+1}$]$^-$ (m+n=3,4; m=0-3, n =0-4) while those of neat AgC$_6$F$_5$ are dominated by the ion

$[Ag(C_6F_5)_2]^-$ and those of neat CuC_6F_5 by $[Cu(C_6F_5)_2]^-$ beside $[Cu(OC_6F_5)(C_6F_5)]^-$ and $[Cu(OC_6F_5)_2]^-$.[15]

Hydrolysis of $Ag(n\text{-}C_4F_9)_2Cu$ (10)

Compounds **9** and **10** appear to be unaffected by water. Stirring of **10** and water or 5% aqueous solution of potassium hydroxide for 8 h gave no evidence of any kind of hydrolysis. However, our attempt to prepare **10** as adduct with triphenylphosphine was accompanied by transformation of the α-CF_2 group into an OCO moiety with final formation of perfluorobutyric acid after acidic working-up procedures. Thus, triphenylphosphine might work as a catalyst for such type of hydrolysis (Scheme 10).

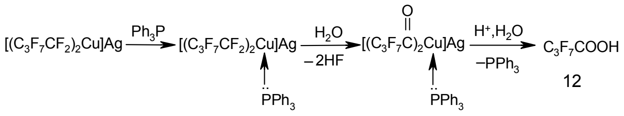
Chemical reactivity of perfluoropropyl (9), perfluorobutyl (10) and perfluorophenyl (11) silver copper couples

Perfluoroorgano silver copper couples **9-11** react with acid halides at ambient temperature for 2 h to give the corresponding ketones in good yields (64-95%) (Scheme 11). We described[16] earlier the preparation of such ketones by the reaction of C_6F_5Ag with acid chlorides that was carried out at 75-80° C for 12 h. This is the advantages of compound **11** over C_6F_5Ag.

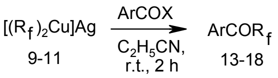
The reaction of couple **9** with 2,4-dinitrochlorobenzene at ambient temperature in propionitrile led to product **19** by substitution of the chlorine atom (Scheme 12).

Our attempts to study the reactions of couples **9** and **10** with 2,4-dinitrochlorobenzene in DMF led only to 2,4,2',4'-tetranitrobiphenyl **19**. The chlorine atom in the 2,4-dinitrobenzene is a very reactive leaving moiety and in DMF, probably, a halogen-copper exchange process takes place; the intermediate formation of a 2,4-dinitrophenylcopper species may forward the diaryl **19**.

Couples **9** and **10** prepared in the propionitrile did not react with aromatic compounds containing electron-donating methyl- or methoxy- groups; but in DMF **10** reacted with 4-bromotoluene or 4-bromoanisole to give 4-perfluorobutylsubstituted aromatic compounds **20** and **21** in 46% and 52% yields correspondingly (Scheme 13).



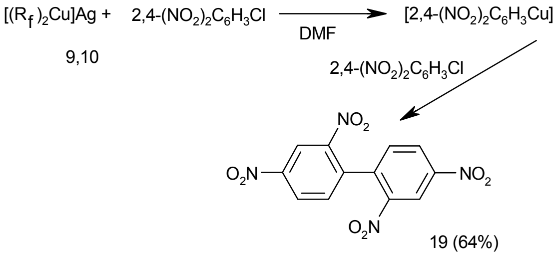
Scheme 10 Hydrolysis of of $Ag(n\text{-}C_4F_9)_2Cu$



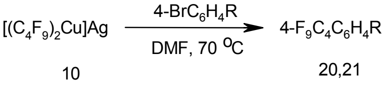
Ar = C_6H_5, X = Br, Cl, R_f = C_3F_7 (13), C_4F_9 (14), C_6F_5 (15)

Ar = 4-$O_2NC_6H_4$, X = Cl, R_f= C_3F_7, (16), C_4F_9 (17), C_6F_5 (18)

Scheme 11 Reaction of silver copper couples (9-11) with organic substrates



Scheme 12 The reaction of couples **9** and **10** with 2,4-dinitrochlorobenzene



R = CH_3 (21), OCH_3 (22)

Scheme 13 Reactions of copper couple **10** with 4-bromotoluene and 4-bromoanisole

Conclusions

In conclusion, an approaches to prepare perfluoroalkyl and pentafluorophenyl copper reagents has been elaborated. Interactions of perfluoroorgano silver compounds and elemental copper gave silver copper couples, $Cu(R_f)_2Ag$, in contrast to trifluoromethyl silver, which interact with elemental copper giving the trifluoromethyl-copper species only.[8a] The silver copper couples **9-11** are stable in solution up to approximately 100 °C and have good chemical reactivity and characterized by easy way of handling.

Experimental section

Fluorine and proton NMR spectra are recordered on a Bruker AC 200 and AMX 300 instruments (^{19}F: 188.3 and ^{1}H: 282.4 MHz respectively) using CCl_3F and TMS as external standard and, unless mentioned, $CDCl_3$ as lock solvent. n-Iodoperfluoroalkanes were purchased from Merck-Schuchardt Co. Solution of n-BuLi in hexane were obtained from Aldrich; silver(I) fluoride from Apollo. All reactions involving organometallic reagents were carried out under an inert atmosphere of pre-purified nitrogen. Ether and tetrahydrofuran were distilled from sodium ketyl immediately before use. N,N-dimethylformamide was freshly distilled under atmospheric pressure prior to use. Cuprous bromide was prepared using the method reported in;[6] trimethyl(perfluoroalkyl)silanes were synthesized from R_fI Me_3SiCl and tetrakis(dimethylamino)ethen following the Petrov procedure;[17] $Me_3SiC_6F_5$ was prepare from Me_3SiCl and $Mg(C_6F_5)Br$ in THF by analogy to.[18] All other starting materials and applied reagents were obtained from Fluka and Merck chemicals.

Perfluoroalkyl lithium/copper couples (4-6). General procedure

To a mixture of the corresponding iodoperfluoroalkane (**1-3**) (5 mmol) and diethyl ether (15 mL) at –95 °C n-BuLi in hexane (5 mL of a 1.6 N solution) was added dropwise under stirring. After stirring at this temperature for 20 min, cuprous bromide (2 mmol) was added and stirring continued for another 25 min followed by dropwise addition of tetrahydrofuran (15 mL) and N,N-dimethylformamide [except compound (**2**)] (15 mL) while the reaction temperature did not exceed –90 °C. The mixture was stirred another 20 min; the composition was monitored by ^{19}F NMR (fluorobenzene as internal standard) spectroscopy at –70 °C (data see Table 1).

Perfluoroalkyl copper (7,8)

Perfluoropropylcopper (**7**) and perfluorobutylcopper (**8**) were obtained from copper powder (12.5 mmol) and corresponding iodoperfluoroalkane (5 mmol) (**2**) and (**3**) in N,N-dimethylformamide (5 mL) as described in[19], method A. ^{19}F NMR spectroscopic data are given in Table 1.

Perfluoroorgano silver copper couples (9-11). General procedure

To the well-stirred mixture of silver fluoride (2 mmol) and propionitrile or DMF (5 mL) at room temperature the corresponding perfluoroalkyl or pentafluorophenyl silane (2 mmol) was added. After stirring for 20 min copper powder (4 mmol) was added and stirring was continued for 4 h. ^{19}F NMR spectroscopic data are summarized in Table 1.

Hydrolysis of the copper couple (10), perfluorobutyric acid (12)

To the copper couple (**10**) obtained in propionitrile as described above was added triphenylphosphine (4 mmol) and water (1 mL). The reaction mixture was stirred at ambient temperature for 12 h and then extracted with 5% aqueous KOH. The aqueous phase was extracted with diethyl ether, filtered and acidified with 2% aqueous sulfuric acid. Perfluorobutyric acid was extracted with diethyl ether, the organic layer was dried with $MgSO_4$ and solvent evaporated.

Yield: (37%), bp 122-123 °C (in capillary by Sivoloboff method), lit. bp 120 °C (735 mm Hg).[20]

^{19}F NMR (200 MHz, $CDCl_3$, $CFCl_3$), δ (ppm): –81.3 (t, $^4J_{F\text{-}F}$ = 9.1 Hz, 3F, CF_3); –120.0 (t, $^4J_{F\text{-}F}$ = 9.1 Hz 2F, α-CF_2); –127.5 (s, 2F, β-CF_2). ^{19}F NMR data match literature values.[21]

Reaction of silver copper couples (9-11) with organic substrates. General procedure

To the silver copper couples (**9-11**) obtained as described above, the corresponding organic substrate (2 mmol) was added. The mixture was stirred at ambient temperature for 2 h (for acid halides) or 6 h (for 2,4-dinitrochlorobenzene) and poured into 2% aqueous sulfuric acid with ice. The organic layer was extracted with diethyl ether. The extract was washed with water and 5% aqueous Na_2CO_3 (for compounds **13-18**), dried over $MgSO_4$, evaporated and the respective product either purified by distillation or crystallization.

Phenyl-n-perfluoropropyl ketone (13)

Colourless liquid*,* yield: (64%), bp 170-172 °C, lit. bp 173.5 °C.[22] ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.56 (t, $^3J_{H\text{-}H}$ = 8 Hz, 2H, Ar-*H-3,5*); 7.70 (t, $^3J_{H\text{-}H}$ = 8 Hz, 1H, Ar-*H-4*) 8.07 (t, $^3J_{H\text{-}H}$ = 10 Hz, 2H, Ar-*H-2,6*). ^{19}F NMR, (200 MHz, $CDCl_3$, $CFCl_3$) δ (ppm): –80.5 (t, $^4J_{F\text{-}F}$ = 9 Hz, 3F, CF_3); –113.9 (m, $^4J_{F\text{-}F}$ = 9 Hz, 2F, α-CF_2); –126.1 (s, 2F, β-CF_2).

Phenyl-n-perfluorobutyl ketone (14)

Colourless liquid, yield: (83%), bp 184-186 °C, lit. bp 188.5 °C.[21] ^{1}H NMR, (300 MHz, $CDCl_3$), δ (ppm): 7.53 (t, $^3J_{H\text{-}H}$ = 8 Hz, 2H, Ar-*H*-3,5); 7.65 (t, $^3J_{H\text{-}H}$ = 8 Hz, 1H, Ar-*H-4*); 8.14 (t, $^3J_{H\text{-}H}$ = 8 Hz, 2H, Ar-*H-2,6*). ^{19}F NMR, (200 MHz, $CDCl_3$, $CFCl_3$) δ (ppm):–81.4 (t, $^4J_{F\text{-}F}$ = 9 Hz, 3F, CF_3); –113.3 (t, $^4J_{F\text{-}F}$ = 10.9 Hz, 2F, α-CF_2,);–125.6 (m, 2F, β-CF_2); –122.2 (m, 2F, γ-CF_2). 2,4-Dinitrophenylhydrazone, mp 133-135 °C (ethanol), lit. mp 133-136 °C.[23]

2,3,4,5,6-Pentafluorobenzophenone (15)

Colourless crystals, yield: (94%), mp 32-33 °C (diethyl ether:pentane 1:1), lit. mp 33-34 °C.[22] ^{1}H NMR, (300 MHz, $CDCl_3$), δ (ppm): 7.51 (t, $^3J_{H\text{-}H}$ = 8 Hz, 2H, Ar-*H-3,5*); 7.67 (t, $^3J_{H\text{-}H}$ = 8 Hz, 1H, Ar-*H-4*); 7.83 (t, $^3J_{H\text{-}H}$ = 8 Hz, 2H, Ar-*H-2,6*). ^{19}F NMR, (200 MHz, $CDCl_3$, $CFCl_3$) δ (ppm):–140.2 (m, 2F, *F-2,6*); –150.8 (m, 1F, *F-4*); –160.2 (m, 2F, *F-3,5*).

4-Nitrophenyl-n-perfluoropropylketone (16)

Colourless crystals, yield: (70%), mp 86-88 °C (pentane). ^{1}H NMR, (300 MHz, $CDCl_3$), δ (ppm): 8.23 (d, $^3J_{H\text{-}H}$ = 6 Hz, 2H, Ar-*H-3,5*); 8.38 (d, $^3J_{H\text{-}H}$ = 6 Hz, 2H, Ar-*H-2,6*). ^{19}F NMR, (200 MHz, $CDCl_3$, $CFCl_3$) δ (ppm): –80.3 (t, $^4J_{F\text{-}F}$ = 5.5 Hz, 3F, CF_3); –114.1 (q, $^4J_{F\text{-}F}$ = 5.5 Hz, 2F, α-CF_2); –125.6 (s, 2F, β-CF_2). ^{1}H and ^{19}F NMR data are identical those the given in.[24]

4-Nitrophenyl-n-perfluoropbutylketone (17)

Colourless crystals*,* yield: (81%), mp 92-94 °C (ether:pentane, 1:1). ^{1}H NMR, (300 MHz, $CDCl_3$), δ (ppm): 8.23 (d, $^3J_{H\text{-}H}$ = 8 Hz, 2H, Ar-*H-3,5*); 8.38 (d, $^3J_{H\text{-}H}$ = 8 Hz, 2H, Ar-*H-2,6*). ^{19}F NMR, (200 MHz, $CDCl_3$, $CFCl_3$) δ (ppm): –81.2 (t, $^4J_{F\text{-}F}$ = 11 Hz, 3F, CF_3); –113.8 (t, $^4J_{F\text{-}F}$ = 11 Hz, 2F, α-CF_2); –122.3 (m, 2F, β-CF_2); –125.6 (m, 2F, γ-CF_2). ^{1}H and ^{19}F NMR data are identical those the given in.[24]

2,3,4,5,6-Pentafluoro-4-nitrobenzophenone (18)

Colourless crystal*,* yield: (95%), mp 122-123 °C (benzene), lit. mp 122-123 °C[25]; 123-124 °C.[16] ^{1}H NMR, (300 MHz, $CDCl_3$), δ (ppm): 8.01 (d, $^3J_{H\text{-}H}$ = 8 Hz, 2H, Ar-*H-3,5*); 8.35 (d, $^3J_{H\text{-}H}$ = 8 Hz, 2H, Ar-*H-2,6*). ^{19}F NMR, (200 MHz, $CDCl_3$, $CFCl_3$) δ (ppm): –139.4 (m, 2F, *F-2,6*); –148.3 (m, 1F, *F-4*); –159.2 (m, 2F, *F-3,5*).

2,4,2′,4′-Tetranitrobiphenyl (19)

Yellow crystals, yield: (64%), mp 143-145 °C (chloroform). ^{1}H NMR, (300 MHz, $CDCl_3$) δ (ppm): 7.88 (d, $^3J_{H\text{-}H}$ = 8 Hz, 1H, Ar-H-6); 8.37 (dd, $^3J_{H\text{-}H}$ = 8 Hz, $^4J_{H\text{-}H}$ = 2.5 Hz, 1H, Ar-*H-5*); 8.70 (d, $^4J_{H\text{-}H}$ = 2.5 Hz, 1H, *H-3*). ^{1}H NMR data are identical those the given in.[26]

Reactions of copper couples (10) with 4-bromotoluene and 4-bromoanisole

To the silver copper couple (**10**) obtained in DMF as described above 4-bromotoluene or 4-bromoanisole (2 mmol) was added. The reaction mixture was stirred at 70-75 °C for 12 h, cooled and poured into 2% aqueous sulfuric acid with ice. The organic layer was extracted with diethyl ether. The extract was washed with water, dried over $MgSO_4$, and evaporated.

4-Perfluoro-n-butyltoluene (20)

Colourless liquid, yield: (46%), bp 187-189 °C (in capillary by Sivoloboff method). ^{1}H NMR, (300 MHz, $CDCl_3$) δ (ppm): 2.41 (s, 3H, CH_3), 7.28 (d, $^3J_{H\text{-}H}$ = 8 Hz, 2H, Ar-*H-3,5*); 7.46 (d, $^3J_{H\text{-}H}$ = 8 Hz, 2H, Ar-*H-2,6*). ^{19}F NMR, (200 MHz, $CDCl_3$, $CFCl_3$) δ (ppm): –81.5 (t, $^4J_{F\text{-}F}$ = 11 Hz 3F CF_3); –107.1 (t, $^4J_{F\text{-}F}$ = 11 Hz, 2F, α-CF_2); –123.3 (m, 2F, β-CF_2); –126.1 (m, 2F, γ-CF_2). ^{1}H and ^{19}F NMR data are identical to those appeared in the literature.[27,28]

4-Perfluorobutylanisole (21)

Colourless liquid, yield: (52%), bp 202-204 °C (in capillary by Sivoloboff method). ^{1}H NMR, (300 MHz, $CDCl_3$) δ (ppm): 3.85 (s, 3H, O-CH_3), 7.40 (d, $^3J_{H\text{-}H}$ = 8 Hz, 2H, Ar-*H-3,5*); 7.51 (d, $^3J_{HH}$ = 8 Hz, 2H, Ar-*H-2,6*). ^{19}F NMR, (200 MHz, $CDCl_3$, $CFCl_3$) δ (ppm): –81.2 (t, $^4J_{FF}$ = 11 Hz 3F, CF_3); –109.4 (t, $^4J_{F\text{-}F}$ = 11 Hz, 2F, α-CF_2,); –121.9 (m, 2F, β-CF_2); –124.9 (m, 2F, γ-CF_2). ^{1}H and ^{19}F NMR data are identical those the given in.[27,28]

Acknowledgements

Generous financial support of this work by the DFG (grant UKR 113) is gratefully acknowledged.

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