Pergamon

TETRAHEDRON

Tetrahedron 58 (2002) 4007–4014

Syntheses, oxidations, and palladium complexes of fluorous dialkyl sulfides: new precursors to highly active catalysts for the Suzuki coupling

Christian Rocaboy and J. A. Gladysz*

Institut für Organische Chemie, Friedrich-Alexander Universität Erlangen-Nürnberg, Henkestrasse 42, 91054 Erlangen, Germany

Received 20 December 2001; revised 30 January 2002; accepted 31 January 2002

Abstract—Reactions of $R_{f8}(CH_2)_nI$ (R_{f8}=$CF_3(CF_2)_7$) with Li_2S give the fluorous dialkyl sulfides $(R_{f8}(CH_2)_n)_2S$ (n=2, **1**, 71%; 3, **2**, 67%) as low melting white solids that are soluble in most fluorous and organic solvents. Reactions of **1** and **2** with CH_3CO_3H yield the corresponding sulfoxides $(R_{f8}(CH_2)_n)_2S{=}O$ (85; 80%), which are soluble in $CF_3C_6F_5$ at room temperature, but insoluble in most other solvents. At higher temperatures, solubilities can become appreciable. Reactions of **1** and **2** with Na_2PdCl_4 (ca. 0.5 equiv.) give palladium complexes $[(R_{f8}(CH_2)_n)_2S]_2PdCl_2$ (**5**, 94%; **6**, 95%), which are soluble in only a limited range of fluorinated solvents at room temperature. The $CF_3C_6F_{11}$/toluene partition coefficients of **1** and **2** are 98.7:1.3 and 96.6:3.4 (24°C). The Suzuki coupling of aryl bromides and $PhB(OH)_2$ to biaryls is catalyzed by **5** and **6** (0.02 mol%) in $CF_3C_6F_{11}$/DMF/H_2O in the presence of K_3PO_4, generally at room temperature. Turnover numbers of 4500–5000 are easily achieved. However, activities decrease under fluorous biphase recycling conditions, and implications for the nature of the catalytically active species are discussed. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Over the past eight years, many new compounds with high affinities for perfluoroalkane and related 'fluorous' solvents have been synthesized.[1,2] This has been prompted by the emergence of 'fluorous biphase chemistry',[1a] a current overview of which is offered by this special issue of *Tetrahedron*. As traditionally implemented, this technique exploits the strongly temperature dependent miscibilities of organic and fluorous solvents.[3] At room temperature, most combinations give two phases.[4] However, with moderate heating, a single phase forms. Reactions can be conducted under monophasic conditions at higher temperatures. Organic products and fluorous catalysts or spent reagents can then be separated under biphasic conditions at lower temperatures. High fluorous phase affinities are achieved by appending sufficient numbers of 'pony tails' of the formula $CF_3(CF_2)_{n-1}(CH_2)_m$ (abbreviated $R_{fn}(CH_2)_m$.

Many applications of fluorous chemistry in catalysis involve metal adducts of organophosphorus[5,6] or nitrogen[7,8] donor ligands. However, sulfur donor ligands also play extensive roles in catalysis. Organosulfur compounds furthermore see widespread use as stoichiometric reagents in organic synthesis.[9] Many of these procedures give organosulfur by-products that are not commonly recycled, usually for lack of a convenient protocol. This intrinsic waste problem and poor atom economy has led to increasing interest in recyclable sulfur reagents.[10,11]

Accordingly, we set out to develop efficient syntheses of simple fluorous dialkyl sulfides, characterize their solubilities and fluorous phase affinities, and explore their basic chemistry. In contrast to fluorous phosphines and amines, only two pony tails are possible in the absence of branching. Thus, slightly lower affinities for fluorous solvents might be expected. We also sought to assay the use of such ligands in catalysis, and describe palladium complexes that are excellent catalyst precursors for the Suzuki coupling—a representative carbon–carbon bond forming reaction of aryl halides.[12] Other types of fluorous organosulfur compounds have been reported,[11,13,14] as well as an elegant fluorous version of the DMSO-based Swern oxidation of alcohols.[11] These are detailed in Section 3.

2. Results

2.1. Syntheses of fluorous compounds

THF solutions of Li_2S were generated as described previously,[15] and treated with the fluorous iodides $R_{f8}(CH_2)_2I$ and $R_{f8}(CH_2)_3I$. The former is commercially available, and the latter is easily synthesized from the corresponding alcohol.[16] As shown in Scheme 1, workups gave the fluorous

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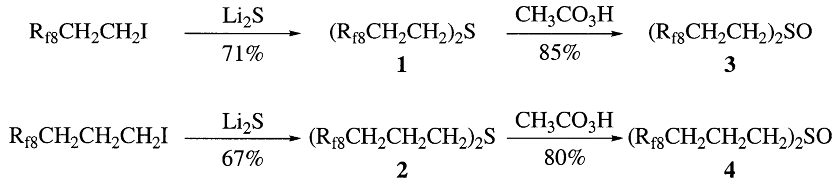
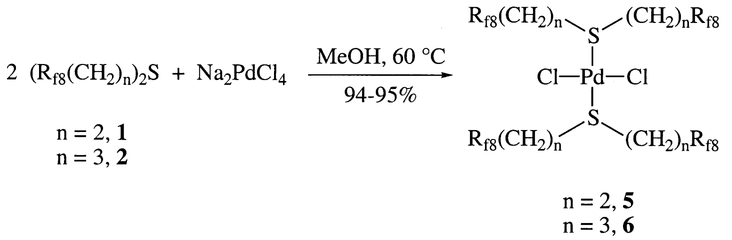
Keywords: sulfides; sulfoxides; Suzuki reactions; catalysis; fluorous chemistry.

* Corresponding author. Tel.: +49-9131-8522540; fax: +49-9131-8526865; e-mail: gladysz@organik.uni-erlangen.de

PII: S0040-4020(02)00275-2



Scheme 1. Syntheses of fluorous dialkyl sulfides and sulfoxides ($R_{f8}=CF_3(CF_2)_7$).



Scheme 2. Syntheses of palladium complexes of fluorous dialkyl sulfides ($R_{f8}=CF_3(CF_2)_7$).

dialkyl sulfides $(R_{f8}CH_2CH_2)_2S$ (**1**) and $(R_{f8}CH_2CH_2CH_2)_2S$ (**2**) in 67–71% yields as analytically pure white solids. DSC measurements[17] showed no phase transitions other than melting (67 and 56°C). Sulfides **1** and **2** were further characterized by NMR spectroscopy (^1H, ^{13}C). They showed good solubility in a broad range of fluorous, 'hemi'-fluorous and non-fluorous solvents, such as $CF_3C_6F_{11}$ (perfluoro(methylcyclohexane)), $CF_3C_6F_5$ (perfluorotoluene), $CF_3C_6H_5$ (α,α,α-trifluorotoluene or 'benzotrifluoride'), hexanes, toluene, $CHCl_3$, CH_2Cl_2, ether, and THF. They were slightly soluble in methanol, ethanol, and acetonitrile.

Sulfides have an extensively developed oxidation chemistry, and fluorous phosphines are easily converted to the corresponding fluorous phosphine oxides.[5d,18] In order to improve our ability to analyze reactions conducted under aerobic conditions below, **1** and **2** were treated with peracetic acid, CH_3CO_3H, under conditions reported to give sulfoxides ($CHCl_3$, room temperature).[19] White powders, presumed to be the target compounds $(R_{f8}CH_2CH_2)_2S{=}O$ (**3**) and $(R_{f8}CH_2CH_2CH_2)_2S{=}O$ (**4**), immediately precipitated (80–85%). Analogous results were obtained with *m*-chloroperbenzoic acid. Correct microanalyses were obtained for these relatively high-melting substances (>123°C), and diagnostic IR ν_{SO} bands were observed (1035 and 1089 cm^{-1}).[20] However, characterization was hampered by their peculiar solubility characteristics.

At room temperature, **3** and **4** were appreciably soluble only in $CF_3C_6F_5$, and slightly soluble in acetic acid and CF_2ClCCl_2F. NMR spectra were recorded in the first two solvents, and **4** was always more soluble than **3**.[21] In contrast, **3** and **4** were insoluble or very poorly soluble in $CF_3C_6F_{11}$, $CF_3C_6H_5$, and organic solvents such as hexanes, toluene, $CHCl_3$, CH_2Cl_2, ether, THF, acetone, methanol, and ethanol. The fluorous sulfoxide $R_{f6}CH_2CH_2S({=}O)CH_3$ ($R_{f6}= CF_3(CF_2)_5$) has been shown to be insoluble in CH_2Cl_2 at low temperature.[11] The solubilities of fluorous compounds can be markedly temperature dependent.[3,22] Accordingly, **3** and **4** were soluble in acetone at 50°C, and slightly soluble in $CF_3C_6F_{11}$, hexanes, toluene, $CHCl_3$, THF, acetone, and ethanol. Solubilities further increased at reflux temperatures, in some cases dramatically.

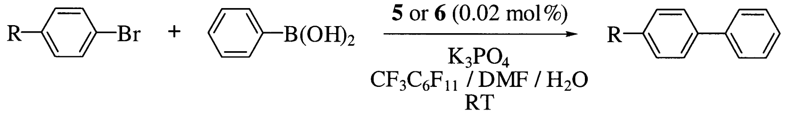
Dupont has recently shown that the palladium bis(sulfide) complex $(Et_2S)_2PdCl_2$ is an effective catalyst precursor for the Suzuki and Heck reactions.[23] We therefore sought palladium derivatives of **1** and **2**. As shown in Scheme 2, reactions with Na_2PdCl_4 gave the target compounds $[(R_{f8}CH_2CH_2)_2S]_2PdCl_2$ (**5**) and $[(R_{f8}CH_2CH_2CH_2)_2S]_2PdCl_2$ (**6**) as analytically pure yellow powders in 94–95% yields. Although *trans*-$(R_2S)_2PdCl_2$ species are usually more stable,[24] *cis* isomers are often isolated and assignments require either single crystals or careful far-IR measurements. As with **3** and **4**, **5** and **6** dissolved in only a very limited range of solvents. They were insoluble in $CF_3C_6F_{11}$, soluble in $CF_3C_6F_5$, and very slightly soluble in $CF_3C_6H_5$. They were insoluble in common organic solvents (hexanes, toluene, $CHCl_3$, CH_2Cl_2, ether, THF, acetone, methanol, and ethanol), failing to impart the slightest hint of color.

Quantitative data on fluorous phase affinities were sought. Accordingly, the $CF_3C_6F_{11}$/toluene partition coefficients of sulfides **1** and **2** were determined by GC as previously reported.[4] These reflect *relative* as opposed to *absolute* solubilities, and are summarized in Table 1. Values for related compounds are given, and analyzed in Section 3. Due to the lack of solubility of sulfoxides **3**, **4** and palladium complexes **5**, **6** in $CF_3C_6F_{11}$ or toluene, analogous partition coefficients could not be determined. However, metal complexes containing more than one fluorous ligand often give partition coefficients higher than the free fluorous ligand.[5d,6g]

Table 1. Partition coefficients (24°C, $R_{f8}=CF_3(CF_2)_7$)

Analyte		$CF_3C_6F_{11}$/toluene
$S(CH_2CH_2R_{f8})_2$	**1**	98.7:1.3[a]
$S(CH_2CH_2CH_2R_{f8})_2$	**2**	96.6:3.4[a]
$HN(CH_2CH_2CH_2R_{f8})_2$	**7**	96.5:3.5[b]
$N(CH_2CH_2CH_2R_{f8})_3$	**8**	>99.7:<0.3[b]
$P(CH_2CH_2R_{f8})_3$	**9**	>99.7:<0.3[c]
$P(CH_2CH_2CH_2R_{f8})_3$	**10**	98.8:1.2[c]

[a] This work.
[b] Ref. 8a.
[c] Ref. 18b.



R[(a)]	Catalyst precursor	Time (h)	Conv (%)[(b)]	Yield (%)[(b)]	TON
$CH_3(C{=}O)$[(c)]	**5**	20	99	93	4650
	6	23	99	90	4500
H	**5**	20	95	94	4700
	6	24	98	95	4750
CH_3O[(c)]	**5**	96	77	71	3550
	6	96	75	69	3450
CH_3[(c,d)]	**5**	68	99	98	4900
	6	67	99	97	4850

(a) Conditions: **5** or **6** (0.0005 mmol), aryl bromide (2.500 mmol), $PhB(OH)_2$ (3.750 mmol), K_3PO_4 (5.000 mmol), $CF_3C_6F_{11}$ (1.00 mL), DMF (3.00 mL), H_2O (2.00 mL), room temperature unless noted. (b) Determined by GC versus hexadecane or tridecane standard. (c) Biphenyl was formed in ca. 8-10% yield based upon $PhB(OH)_2$. (d) 50 °C.

Chart 1. Suzuki coupling with catalyst precursors **5** and **6**.

2.2. Catalysis

Fluorous palladium complexes **5** and **6** were assayed as catalyst precursors for the Suzuki reaction, using a standard set of conditions.[12,23a] As summarized in Chart 1, suspensions of **5** or **6** in $CF_3C_6F_{11}$ were sequentially treated with DMF, an aryl bromide (1.0 equiv.), phenylboronic acid ($PhB(OH)_2$, 1.5 equiv.), and an aqueous solution of the base K_3PO_4. Both **5** and **6** (present at 0.02 mol%) dissolved, and the two-liquid-phase systems were vigorously stirred at room temperature unless noted. In accord with other recent studies,[25] no efforts were made to exclude air. The biaryl products precipitated during the reactions, providing a qualitative measure of conversion. No black precipitate or other sign of palladium metal formation was observed.

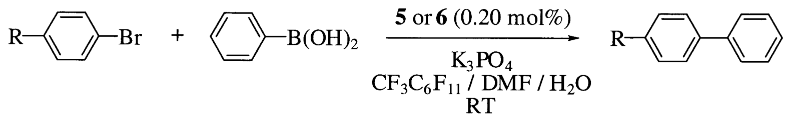
After workup via ether extraction, reactant conversions and product yields (based upon the limiting aryl bromide) were determined by GC versus internal standards. Both **5** and **6** gave comparable results. The reactions of *p*-bromoacetophenone and bromobenzene were essentially complete after 24 h at room temperature. The reactions of *p*-bromoanisole and *p*-bromotoluene were slower, consistent with electronic effects upon reactivity noted earlier,[12,23a] and the latter was conducted at 50°C.

For three aryl bromides, the yields of the target biaryls were greater than 90%. For the fourth (*p*-bromoanisole), the yields (71–69%) were only slightly lower than the conversions (77–75%). This implies that yields of ca. 90% would be attained with higher temperatures and/or longer reaction times. Minor amounts of biphenyl, a homocoupling product of the boronic acid, were observed in some cases. More importantly, turnover numbers approached 5000, indicating a long-lived catalyst system with excellent prospects for further optimization.

We next sought to probe whether the catalytically active species or a precursor could be recycled. Thus, analogous reactions were conducted with a ten-fold higher, 0.2 mol%, palladium loading. Toluene was then added to give a three-liquid-phase organic/aqueous/fluorous system. The upper two layers were removed, and the denser fluorous phase was extracted with toluene. GC analysis as above showed comparable conversions and yields, as summarized in Chart 2. However, all reactions were much faster, consistent with the higher loadings.

The recovered fluorous phase was charged with fresh reactants. A second cycle of catalysis could always be observed (Chart 2). However, turnover frequencies diminished, as evidenced by the slower precipitation of biaryl products, and in most cases lower conversions and yields after reaction times distinctly longer than those of the first cycles. When third cycles were conducted, much longer times were needed, and yields often deteriorated further. When any given run was allowed to proceed significantly past complete conversion, it turned gray and then the characteristic color of palladium black.

Various scenarios consistent with the preceding behavior are analyzed in Section 3. To help narrow the possibilities, the first cycle of the first reaction in Chart 2 was repeated (*p*-bromoacetophenone, catalyst **5**), and the product-containing toluene extracts were charged with fresh *p*-bromoacetophenone, $PhB(OH)_2$, DMF, and an aqueous solution of K_3PO_4. The reaction was closely monitored by GC, and after 5.5 h—much longer than the times required for cycles 1 or 2—conversion to the biaryl product was complete. Next, the toluene extract from an identical experiment was treated with aqueous KOH. This system was extracted with ether and analyzed by ^{19}F NMR in the presence of an internal standard. The fluorous sulfide **1** was the only species detected (10–15% of the ligand present in catalyst **5**; range for two runs).



$R^{(a)}$	Catalyst	Cycle	Time	Conv (%)$^{(b)}$	Yield (%)$^{(b)}$	TON$^{(c)}$
$CH_3(C{=}O)^{(d)}$	**5**	1	4.5 min	100	99	500
		2	12 min	100	99	1000
		3	270 min	70	69	1345
	6	1	5 min	100	99	500
		2	15 min	90	89	945
		3	270 min	97	97	1430
H	**5**	1	0.5 h	97	94	470
		2	3 h	85	81	885
		3	24 h	85	85	1310
	6	1	0.5 h	90	87	435
		2	2.5 h	74	74	805
		3	19 h	84	84	1225
$CH_3O^{(d)}$	**5**	1	0.5 h	99	96	480
		2	25 h	80	74	850
	6	1	0.5 h	96	86	430
		2	20 h	76	65	755
$CH_3^{(d,e)}$	**5**	1	5 min	100	99	500
		2	75 min	80	77	885
		3	24 h	53	45	1110
	6	1	10 min	100	97	485
		2	75 min	78	78	875
		3	24 h	47	46	1105

(a) Conditions: **5** or **6** (0.0020 mmol), aryl bromide (1.00 mmol), $PhB(OH)_2$ (1.50 mmol), K_3PO_4 (2.00 mmol), $CF_3C_6F_{11}$ (1.50 mL), DMF (2.00 mL), H_2O (1.50 mL), room temperature unless noted. (b) Determined by GC versus hexadecane or tridecane. (c) Cumulative. (d) Biphenyl was formed in ca. 2-8% yield based upon $PhB(OH)_2$. (e) 50 °C

Chart 2. Recycling of Suzuki catalysts derived from **5** and **6**.

3. Discussion

Scheme 1 establishes that fluorous primary iodides with at least two methylene spacers are easily converted to the corresponding fluorous dialkyl sulfides and sulfoxides. Closely related sequences leading to sulfides and sulfoxides of the type $R_{fn}(CH_2)_2S(X)CH_3$ (n=4, 6; R_{fn}=$CF_3(CF_2)_{n-1}$) have been recently reported by Crich.[11] A lower homolog of **1**, $(R_{f6}CH_2CH_2)_2S$, has been sketchily described, together with other $R_{f6}CH_2CH_2SR$ species.[13a] Portella has prepared various fluorous sulfides with one methylene spacer, $R_{fn}CH_2SR$, from fluorous tosylates,[13b] and analogs without methylene spacers are known.[13g] Several fluorous thiols and disulfides have been synthesized,[13] and two thiols have recently become commercially available. Hence, despite a somewhat scattered preparative literature, a wide variety of fluorous organosulfur compounds are now readily available. Applications as scavengers in high-throughput syntheses are described elsewhere in this issue.[26]

The compounds in Scheme 1 are also important because their physical properties can be compared to those of many closely related fluorous compounds. The sulfoxides and palladium complexes **3**–**6** are simply too insoluble for conventional partition coefficient measurements. However, as shown in Table 1, the partition coefficients of sulfides **1** and **2** indicate very high fluorous phase affinities. They are slightly lower than those of analogous tertiary amines and phosphines with three pony tails (**1** vs **9**; **2** vs **8** and **10**). However, they would be expected to reach >99:<1 with longer, R_{f10}-containing pony tails.[18a] The sulfide **2** can also be directly compared to secondary amine $HN((CH_2)_3R_{f8})_2$ (**7**), which differs only by a HN/S replacement. Interestingly, the partition coefficients are very close (96.6:3.4 vs 96.5:3.5).

Although none of our data bear upon the electronic properties of sulfides and sulfoxides **1**–**4**, they can be expected to be less electron rich than analogous compounds with n-alkyl substituents. Detailed studies of fluorous aliphatic amines[8a] and phosphines[18,27] show that the electron withdrawing effect of the R_{f8} group has a significant effect upon solution-phase equilibria and spectroscopic properties through five methylene groups (inclusive). With gas-phase vertical ionization potentials, about ten methylene groups are required before an asymptotic limit is reached.[27]

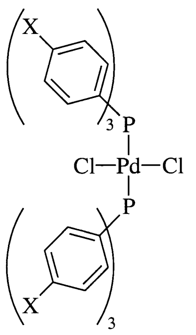
The data in Charts 1 and 2 show that palladium complexes **5** and **6** are effective catalyst precursors for the Suzuki reaction. We are particularly struck by the mild conditions and TON values in Chart 1. As recently as 1999, the scarcity of ambient-temperature couplings of aryl bromides and $PhB(OH)_2$ was a point of emphasis.[12c,28] In the course of another project involving new catalysts for the Suzuki reaction,[29] we have measured rates of a benchmark high-activity system, 1:4 $Pd(OAc)_2/P(t\text{-}Bu)_3$ in toluene at 80–100°C (1 mol% palladium, K_3PO_4).[28,30] The catalyst system in Chart 1 is distinctly faster.

This in turn poses the question of the active catalyst. The recycling data in Chart 2 show a progressive loss of activity (rate or turnover frequency (TOF)) that is consistent with at least four possibilities: (1) the generation of a homogeneous fluorous catalyst that is not very efficiently recycled (modest partition coefficient or fluorous phase solubility); (2) the generation of a homogeneous fluorous catalyst that is efficiently recycled but gradually deactivated; (3) the generation of a non-recyclable heterogeneous or metallic catalyst at a slow rate from a homogeneous precursor, with recycling of the remaining precursor until it becomes exhausted; (4) the generation of a fluorous heterogenous or metallic catalyst that is not very stable or efficiently recycled.

The eventual appearance of metallic palladium under the conditions of Chart 2 leads us to favor possibilities three and/or four. Dupont also reported that $(Et_2S)_2PdCl_2$ gives palladium black under certain Suzuki conditions.[23a] The significant leaching of fluorous sulfide ligand **1** (10–15% of theory) is consistent with all four scenarios, although we emphasize that our analysis does not identify the *primary* species *first* transported to the non-fluorous phase. The markedly attenuated catalytic activity of the product-containing organic phases suggests lower levels of active catalyst, although palladium in catalytically inactive forms may of course be present.

Various types of heterogeneous or metallic palladium species are known to be highly active catalysts for the Suzuki and Heck reactions.[31–36] The so-called 'ligand free' catalysts constitute one intensively investigated category.[31,32] However, analyses are complicated by recent evidence that heterogeneous palladium species can under some conditions serve as precursors to homogeneous palladium catalysts.[34] Furthermore, two distinct types of fluorous-phase-soluble palladium nanoparticles have been reported.[35,36] Both catalyze the Suzuki and Heck reactions, and can to varying extents be recycled. One is stabilized by a fluorous derivative of the enone ligand $O{=}C(CH{=}CHC_6H_5)_2$, raising the possibility of a similar role for the fluorous sulfide ligands.[36b]

In very relevant recent work, Bannwarth has reported that the palladium fluorous phosphine complexes **11**–**12** are good catalyst precursors for the Suzuki reaction.[61] At 1.5 mol% palladium loadings, high yields were obtained through six cycles for a variety of substrates. However, at 0.1 mol% loadings, rates and yields dropped for the second cycle, and had markedly decreased by the fourth cycle. Hence, the fluorous phosphine and fluorous dialkyl sulfide-based systems show similar characteristics. As recognized by Bannwarth[61] and emphasized in a recent critical analysis,[37] recycling efficiency is best quantified by measuring rate (or TOF) as a function of cycle. When the time selected for the first cycle is unnecessarily long, comparable yields can be obtained for subsequent cycles, even when recycling is only moderately efficient.



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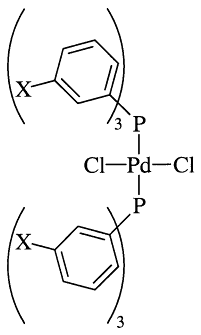

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X = a) R_{f8}
b) $R_{f8}CH_2CH_2$

Independent of recycling efficiency, there are various ways to probe whether the catalysis in Charts 1 and 2 is due to a homogeneous species, heterogeneous species, or a mixture thereof. However, such efforts do not always converge upon a unique answer, even after intensive study. The aerobic conditions would necessitate additional control experiments. Thus, our plan is to develop second-generation fluorous catalyst precursors with multidentate ligands, such as cyclometalated species.[38] These are often thought to be less readily detached during a catalytic cycle, thereby helping to preserve catalyst integrity. Hence, the data in Charts 1 and 2 can be regarded as a baseline by which the performance of these new systems can be measured.

In summary, this study has established convenient and practical syntheses of simple symmetrical fluorous dialkyl sulfides and sulfoxides. Palladium complexes of the former are precursors to highly active catalysts for the Suzuki coupling, the characterization and optimization of which is ongoing. New catalyst systems based upon fluorous cyclometalated sulfur and nitrogen donor ligands will be described in the near future.[39]

4. Experimental

4.1. General

Reactions were conducted in air with reagent grade solvents unless noted. The reagents $CF_3(CF_2)_7CH_2CH_2I$ ($R_{f8}CH_2CH_2I$), bromobenzene, *p*-bromoacetophenone, *p*-bromoanisole, *p*-bromotoluene, $PhB(OH)_2$, K_3PO_4

(7×Aldrich), Na_2PdCl_4 (Strem), $LiEt_3BH$ (Acros), CH_3CO_3H (39% in acetic acid; Fluka) were used as received. NMR spectra were recorded on Bruker or Jeol 400 MHz spectrometers at ambient probe temperature and referenced to residual internal $CHCl_3$ (^1H, δ 7.27) or $CDCl_3$ (^{13}C, δ 77.2), or external $CFCl_3$ (^{19}F, δ 0.00). IR spectra were measured on an ASI React-IR spectrometer. Gas chromatography was conducted on a ThermoQuest Trace GC 2000 instrument. DSC data were recorded with a Mettler–Toledo DSC821 instrument and treated by standard methods.[17] Elemental analyses were conducted with a Carlo Erba EA1110 instrument.

4.1.1. Bis(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)sulfide or $(R_{f8}CH_2CH_2)_2S$ (1). A Schlenk flask was charged with sulfur (0.058 g, 1.809 mmol) under N_2, and $LiEt_3BH$ (1.0 M in THF; 3.80 mL, 3.80 mmol) was added dropwise with stirring over 15 min.[15] After 20 min, a solution of $R_{f8}CH_2CH_2I$ (2.080 g, 3.624 mmol) in dry THF (10 mL, distilled from Na/benzophenone) was added dropwise. The yellow solution quickly decolorized, and was stirred overnight. Water (10 mL) and then aqueous KOH (10 mL, 1 M) were added. The mixture was extracted with ether (3×20 mL) and dried ($MgSO_4$). The volatiles were removed by rotary evaporation. The residue was purified by column chromatography (silica gel, hexanes/EtOAc, 9:1 v/v). The solvent was removed by rotary evaporation and oil pump vacuum to give **1** as a white solid (1.191 g, 1.285 mmol, 71%), mp 67 (capillary), 66.9 (DSC)°C. Calcd for $C_{20}H_8F_{34}S$: C, 25.93; H, 0.76. Found: C, 25.85; H, 0.76. NMR (δ, $CDCl_3$): ^1H 2.34–2.47 (m, $2CH_2CF_2$), 2.79 (t, $^3J_{HH}$=8 Hz, $2SCH_2$); $^{13}C\{^1H\}$ (partial) 23.1 (t, $^3J_{CF}$=5 Hz, $2SCH_2$), 32.1 (t, $^2J_{CF}$=22 Hz, $2\mathit{C}H_2CF_2$); ^{19}F −81.1 (t, $^3J_{HH}$=11 Hz, $2CF_3$), −113.3 (br s, $2CF_2$), −122.3 (br s, $6CF_2$), −123.0 (br s, $2CF_2$), −123.7 (br s, $2CF_2$), −125.3 (br s, $2CF_2$).

4.1.2. Bis(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)sulfide or $(R_{f8}CH_2CH_2CH_2)_2S$ (2). Sulfur (0.052 g, 1.622 mmol), $LiEt_3BH$ (3.50 mL, 3.50 mmol), $R_{f8}CH_2CH_2CH_2I$ (2.012 g, 3.421 mmol), and THF (15 mL) were combined in a procedure analogous to that for **1**. A nearly identical workup (silica gel chromatography with hexanes and then ether) gave **2** as a white solid (1.051 g, 1.101 mmol, 67%), mp 56 (capillary), 56.5 (DSC)°C. Calcd for $C_{22}H_{12}F_{34}S$: C, 27.69; H, 1.26. Found: C, 27.83; H, 1.22. NMR (δ, $CDCl_3$): ^1H 1.88–1.99 (m, $2C\mathit{H}_2CH_2CF_2$), 2.19–2.30 (m, $2CH_2C\mathit{H}_2CF_2$), 2.62 (t, $^3J_{HH}$=8 Hz, $2SCH_2$); $^{13}C\{^1H\}$ (partial) 20.4 (s, $2\mathit{C}H_2CH_2CF_2$), 30.0 (t, $^2J_{CF}$=22 Hz, $2\mathit{C}H_2CF_2$), 31.3 (s, $2SCH_2$).

4.1.3. Bis(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)sulfoxide or $(R_{f8}CH_2CH_2)_2S{=}O$ (3). A round bottom flask was charged with **1** (0.380 g, 0.410 mmol) and $CHCl_3$ (12 mL). Then CH_3CO_3H (39% in acetic acid; 0.100 mL, 0.513 mmol) was added with stirring.[18] A white precipitate formed immediately. After 15 min, the precipitate was collected by filtration, washed with ether (3×10 mL), and dried by oil pump vacuum to give **3** as a white solid (0.328 g, 0.348 mmol, 85%), mp 140 (capillary), 140.7 (DSC)°C. Calcd for $C_{20}H_8F_{34}SO$: C, 25.49; H, 0.85. Found: C, 25.49; H, 0.92. IR (powder, cm^{-1}): ν_{SO} 1035 m. NMR (δ, $CDCl_3/CF_3C_6F_5$, 2:1 v/v): ^1H 2.65–2.80 (m, $2C\mathit{HH'}CF_2$), 3.00–3.12 (m, $2SC\mathit{HH'}$), and virtually identical in CD_3CO_2D (2.70–2.88, 3.28–3.40); $^{13}C\{^1H\}$ (partial) 25.5 (t, $^2J_{CF}$=22 Hz, $2\mathit{C}H_2CF_2$), 44.1 (s, $2SCH_2$).

4.1.4. Bis(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)sulfoxide or $(R_{f8}CH_2CH_2CH_2)_2S{=}O$ (4). Sulfide **2** (0.219 g, 0.229 mmol), $CHCl_3$ (6 mL), and CH_3CO_3H (0.055 mL, 0.285 mmol) were combined in a procedure analogous to that for **3**. An identical workup gave **4** as white solid (0.177 g, 0.182 mmol, 80%), mp 123 (capillary), 124.5 (DSC)°C. Calcd for $C_{22}H_{12}F_{34}SO$: C, 27.23; H, 1.24. Found: C, 27.05; H, 1.46. IR (powder, cm^{-1}): ν_{SO} 1089 m. NMR (δ, $CDCl_3/CF_3C_6F_5$, 3:1 v/v): ^1H 2.20–2.43 (m, $2C\mathit{HH'}C\mathit{HH'}CF_2$), 2.83, 2.85 (two overlapping dt appearing as an octet; $^2J_{HH}$=20 Hz, $^3J_{HH}$=7 Hz, $2SC\mathit{H}H'$ and $2SCH\mathit{H'}$); $^{13}C\{^1H\}$ (partial) 15.0 (s, $2\mathit{C}H_2CH_2CF_2$), 30.3 (t, $^2J_{CF}$=22 Hz, $2\mathit{C}H_2CF_2$), 51.9 (s, $2SCH_2$).

4.1.5. $[(R_{f8}CH_2CH_2)_2S]_2PdCl_2$ (5). A round-bottom flask was charged with **1** (0.423 g, 0.456 mmol), Na_2PdCl_4 (0.059 g, 0.200 mmol), and MeOH (7 mL). The brown mixture was immersed in a 60°C oil bath (melting and dissolution of **1**). A yellow precipitate rapidly formed. The mixture was stirred (1 h) and allowed to cool to room temperature. The precipitate was collected on a fritted funnel, washed with water (3×10 mL), MeOH (3×10 mL), and ether (3×10 mL), and dried by oil pump vacuum to give **5** as a light yellow solid (0.381 g, 0.188 mmol, 94%), mp 178–179 (capillary), 177.1 (DSC)°C. Calcd for $C_{40}H_{16}F_{68}Cl_2S_2Pd$: C, 23.67; H, 0.79. Found: C, 23.83; H, 1.01. NMR (δ, $CDCl_3/CF_3C_6F_5$, 1:1 v/v): ^1H 2.80–2.87 (m, $4CH_2CF_2$), 3.28 (br s, $4SCH_2$). MS (*m*/*z*, positive FAB) 1032 ($Pd(\mathbf{1})^+$, 100%).

4.1.6. $[(R_{f8}CH_2CH_2CH_2)_2S]_2PdCl_2$ (6). Sulfide **2** (0.973 g, 1.019 mmol), Na_2PdCl_4 (0.136 g, 0.462 mmol), and MeOH (15 mL) were combined in a procedure analogous to that for **5**. An identical workup gave **6** as a light yellow solid (0.917 g, 0.440 mmol, 95%), mp 153–154 (capillary), 155.6 (DSC)°C. Calcd for $C_{44}H_{24}F_{68}Cl_2S_2Pd$: C, 25.33; H, 1.16. Found: C, 25.64; H, 1.40. NMR (δ, $CDCl_3/CF_3C_6F_5$, 1:1 v/v): ^1H 2.30–2.63 (m, $4C\mathit{H}_2C\mathit{H}_2CF_2$), 3.15 (br s, $4SCH_2$); $^{13}C\{^1H\}$ (partial) 20.3 (s, $4\mathit{C}H_2CH_2CF_2$), 30.5 (t, $^2J_{CF}$= 22 Hz, $4\mathit{C}H_2CF_2$), 38.3 (s, $4SCH_2$). MS (*m*/*z*, positive FAB) 1061 ($Pd(\mathbf{2})^+$, 100%).

4.2. Catalysis; general procedure

A 25 mL round bottom flask was charged with a Teflon stir bar, **5** or **6** (0.0010 g, 0.0005 mmol), and $CF_3C_6F_{11}$ (1.00 mL). Then DMF (3.00 mL), an aryl bromide (2.500 mmol), $PhB(OH)_2$ (0.724 g, 3.750 mmol), and a solution of K_3PO_4 (1.016 g, 5.000 mmol) in water (2.00 mL) were added. The samples were vigorously stirred at room temperature (50°C for *p*-bromotoluene) for the time specified in Chart 1. Then ether (10 mL) and aqueous KOH (10 mL, 1 M) were added. The ether layer was separated, and the aqueous layer was extracted twice more with ether (10 mL). The extracts were dried ($MgSO_4$) and analyzed by GC using hexadecane or tridecane standard (Chart 1). Authentic samples of all products were purchased from Aldrich.

4.3. Recycling; general procedure

A tube was charged with a Teflon stirring bar, **5** or **6** (0.0041 g, 0.0020 mmol), and $CF_3C_6F_{11}$ (1.50 mL). Then a stock DMF solution (2.00 mL) that was 0.50 M in aryl bromide (1.00 mmol) and 0.75 M in $PhB(OH)_2$ (1.50 mmol) was added, immediately followed by aqueous K_3PO_4 (1.33 M; 1.50 mL, 2.00 mmol). Reactions were conducted as in the previous procedure for the times specified in Chart 2. Stirring was then halted and toluene added (2.00 mL), giving a three phase system. The two upper layers were carefully removed via syringe, and the bottom fluorous phase extracted once more with toluene (2.00 mL). The tube with the fluorous phase was recharged with the DMF solution of aryl bromide and $PhB(OH)_2$ (2.00 mL), and then the aqueous solution of K_3PO_4 (1.50 mL). An identical second cycle was conducted. The upper toluene/water layers were treated with aqueous KOH and ether as in the previous procedure, and analyzed by GC (Chart 2).

4.4. Leaching tests

A. A tube was charged with **5** (0.0041 g, 0.0020 mmol), $CF_3C_6F_{11}$ (1.50 mL), a stock DMF solution (2.00 mL) that was 0.50 M in *p*-bromoacetophenone (1.00 mmol) and 0.75 M in $PhB(OH)_2$ (1.50 mmol), and aqueous K_3PO_4 (1.33 M; 1.50 mL, 2.00 mmol) as in the previous experiment. An identical reaction and workup gave a toluene extract, which was recharged in a second tube with the DMF solution of *p*-bromoacetophenone and $PhB(OH)_2$ (2.00 mL), and the aqueous K_3PO_4 (1.50 mL). The biphasic mixture was vigorously stirred. GC data: see text. *B*. A tube was charged with the same materials as the previous experiment. After 5 min, stirring was halted and toluene added (2.00 mL), giving a three phase system. The two upper layers were carefully removed via syringe, and the bottom fluorous phase extracted once more with toluene (2.00 mL). The upper toluene/water layers were treated with ether (10 mL) and aqueous KOH (10 mL, 1 M). The organic layer was dried ($MgSO_4$) and taken to dryness. The white residue was taken up in $CDCl_3$ (2.50 mL), and a solution of $CF_3C_6H_5$ in $CDCl_3$ (0.041 M; 0.100 mL, 0.0041 mmol) was added. A ^{19}F NMR spectrum showed only **1**, and integration of the CF_3 signal versus that of the standard (δ −81.1 ($2CF_3$) vs −63.0) indicated 0.0004–0.0006 mmol to be present (two runs; 10–15% of theory).

4.5. Partition coefficients

The following is representative. A 10 mL vial was charged with **1** (0.0303 g, 0.0327 mmol), $CF_3C_6F_{11}$ (2.000 mL; distilled from P_2O_5), and toluene (2.000 mL; distilled from Na/benzophenone), equipped with a mininert valve, vigorously shaken (2 min). After 1 h, a 0.500 mL aliquot of each layer was added to 0.250 mL of a standard 0.100 M solution of hexadecane in toluene. The solutions were diluted with ether (4.00–5.00 mL). GC analysis (average of 5–6 injections) showed that 0.00755 mmol of **1** was in the $CF_3C_6F_{11}$ aliquot and 0.00010 mmol in the toluene aliquot (98.7:1.3; a 2.000/0.500 scale factor gives a total mass recovery of 0.0283 g, 93%).

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft (DFG; GL 301/3-1) and Johnson Matthey PMC (palladium loan) for support.

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