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Improved synthesis, structure, and reactivity of 1,4-bis(trimethylsilyl)octafluorobutane

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ABSTRACT

A new high-yielding protocol to prepare 1,4-bis(trimethylsilyl)octafluorobutane (**1**) on a multi-gram scale was realized. The relatively high melting point of **1** facilitated the determination of its single crystal X-ray structure. Reactivity studies determined that, under conditions tested thus far, compound **1** was prone to form $H(CF_2)_4H$ upon reaction with fluoride and alkoxide sources faster than reacting with various acceptor substrates. However, reaction of **1** with silver fluoride in the presence of $[(PPh_3)_3CuCl]$ led to the formation of the bis-cuprate $[Cu_2(C_4F_8)_2]$ dianion and two of the unique $[(PPh_3)_3Ag\text{-}ClAg(PPh_3)_3]$ counter-cations.

1. Introduction

Perfluoroalkylsilane reagents are amongst the most versatile building blocks for introducing a perfluoroalkyl group into organic and organometallic substrates [1–4]. The ability of an initiator like fluoride to attack the silicon atom in these reagents conveniently produces *in situ* a more nucleophilic source of the perfluoroalkyl group, which can be used in a variety of synthetically useful transformations. In this way, perfluoroalkyl groups can undergo formal nucleophilic additions to ketones, aldehydes, and imines (Scheme 1, Eqs. (a) and (b)) [2,4,5]. Perfluoroalkyl groups may also be transferred from silicon to a transition metal catalyst like copper or palladium with the help of an initiator, which enables the perfluoroalkylation of aryl chlorides, bromides, and iodides (Scheme 1, Eq. (c)) [6–9]. It is also well-known that stable and well-defined transition-metal perfluoroalkyl complexes may also be prepared [7,8,10,11], many of which are derived from perfluoroalkylsilane reagents (for example, Eqs. (d–e)). The first use of perfluoroalkylsilane as a vehicle to transfer a perfluoroalkyl group to a transition metal was reported by Fuchikami in 1991 who showed that a copper(I)-CF_3 source could be generated from the combination of trimethyl(trifluoromethyl)silane, copper iodide, and potassium fluoride [12].

Since then, the formation of longer (non-CF_3) perfluoroalkyl metal complexes from perfluoroalkylsilane reagents (Scheme 1, Eqs. (d) and (e) has much precedent [13–18]. However, there is no report of using disilylated perfluoroalkanes to prepare metallacyclopentanes as described in Scheme 1, Eq. (f). The perfluorometallacyclopentane derivatives have, to date, only been prepared by the oxidative coupling of tetrafluoroethylene or through the use of recently reported dizinc reagents [19]. An approach to metallacyclic complexes using disilylated perfluoroalkane reagents would be desirable, as the silyl complexes have a longer shelf life than the perfluoroalkyl zinc reagents. However, disilylated perfluoroalkane reagents themselves have little precedence in the literature. In 1969, Jukes and Gilman reported the synthesis of 1,4-bis(trimethylsilyl)octafluorobutane (**1**) by the reaction of 1,4-dibromooctafluorobutane with Mg and TMS-Cl (TMS = trimethylsilyl) [20]. In that report, only a scant experimental procedure, which did not include any NMR spectroscopy data, was provided. In our hands, Jukes and Gilman's Grignard-based protocol to prepare **1** proved unreliable, so we explored alternative methods for its preparation.

2. Results and discussion

We found that the protocol based on Ruppert's initial synthesis [21,22] of TMS-CF_3 as described in Eq. (1) provided the highest and most consistent yields of **1**. Using this method, **1** can be prepared on a multi-gram scale (12 g prepared in this report) to

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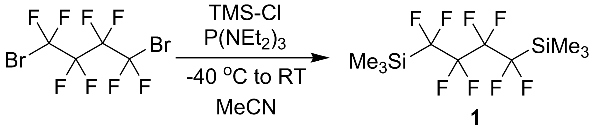
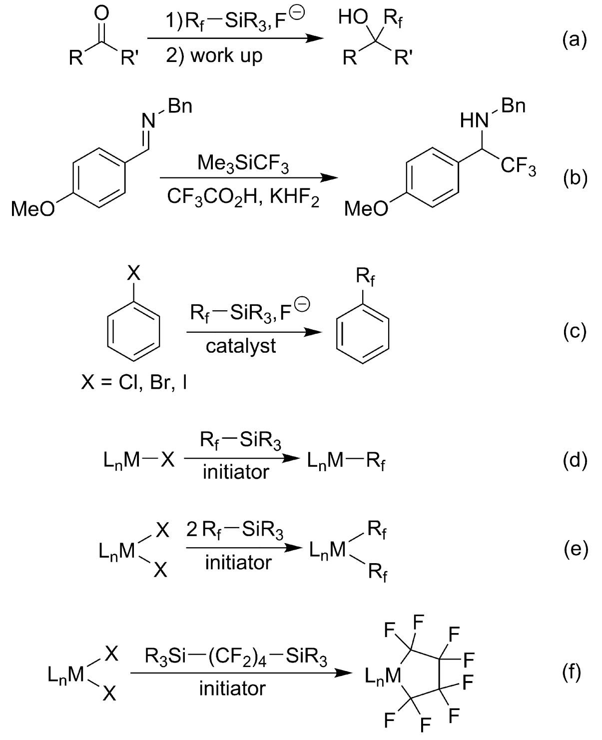
yield pure product in 70% yield after vacuum distillation.



(1)(1)

Because of the lack of crystallinity of many perfluoroalkyl silanes, reports of crystal structures are rare [23–28]. The structure of trimethyl(trifluoromethyl)silane, for instance, could only be obtained through high pressure freezing in a diamond anvil cell [25] or by use of an optical heating and crystallization device [26]. Compound **1**, however, is a higher melting solid (melting point of 28–29 °C),[20] and crystals grown from slowly cooling a melt of **1** could be quickly mounted on a diffractometer equipped with a standard low temperature cooling device. The result of the X-ray data collection is described in Fig. 1. Compound **1** crystallizes in the $P2_12_12_1$ space group, with two molecules in the asymmetric unit. The Si–C_{CF3} bond lengths of all the molecules in the unit cell average to 1.942(19) Å, which is similar to the Si–C_{CF3} bond length of 1.943(12) that was determined experimentally for trimethyl(trifluoromethyl)silane by Olejniczak and co-workers [25]. Woski and co-workers determined a much shorter Si–C_{CF3} bond length of 1.917(5) Å for trimethyl(trifluoromethyl)silane, but this value was much different than those derived from gas phase calculations (1.948 Å for Hartree Fock and 1.937 Å for MP2) and microwave spectroscopy/gas electron diffraction techniques (1.941(3) Å) [26].

With access to large quantities of compound **1** in hand, its reactivity was explored. Despite numerous attempts to prepare a perfluorometallocyclic compound (Scheme 1, f), or to use **1** in a perfluoroalkylation reaction, all of our efforts failed. For instance, when **1** was subjected to conditions commonly employed for transmetalation or perfluoroalkylation reactions (Scheme 2) [17,19,29], the major identifiable fluorine-containing species detected in all cases was 1,1,2,2,3,3,4,4-octafluorobutane. We have thus far been unable to use **1** to prepare the known $[(MeCN)_2Ni(C_4F_8)]$ [19], to perfluoroalkylate 2,3-diiodopyridine to form the known 5,5,6,6,7,7,8,8-octafluoro-5,6,7,8-tetrahydroquinoline [19], or to achieve dicupration with $[Cu(O^tBu)]_4$ and phenanthroline [29]. We speculate that the presence of a nearby silicon atom to transiently generated perfluoroalkyl nucleophile might lead to species **2** (Eq. (2)), which then rapidly decomposes to H(CF2)4H. Such a reaction has precedence in the literature, as it was independently shown by two research groups [24,30] that the trifluoromethyl derivative of the pentacoordinate silicon species **3** decomposes at temperatures as low as −60 °C to lose fluoroform (Eq (3)). We have evaluated the decomposition of **1** in the presence of the two initiators CsF and $[NBu_4]F$, and determined that the counter cation plays a large role in the decomposition. When **1** was reacted with two equivalents of CsF in DMF solvent, TMS-F was formed in 73% yield, but neither other fluorine-containing species nor starting material was detected in appreciable amount in solution. In contrast, when **1** was reacted with two equivalent of $[NBu_4]F$ in THF solvent, $H(CF_2)_4H$ was formed cleanly in 85% yield. The generation of $H(CF_2)_4H$ also proceeded in high yields (65%) when a sub-stoichiometric amount (20%) of $[NBu_4]F$ was used, indicating that a chain mechanism (intermolecular) similar to that seen for TMS-CF_3 (Eq. (3)) may also be operative.



Scheme 1. Selected transformations involving perfluoroalkyl groups derived from perfluoroalkylsilane reagents.

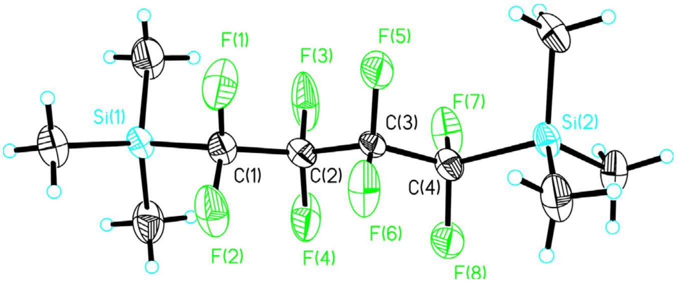
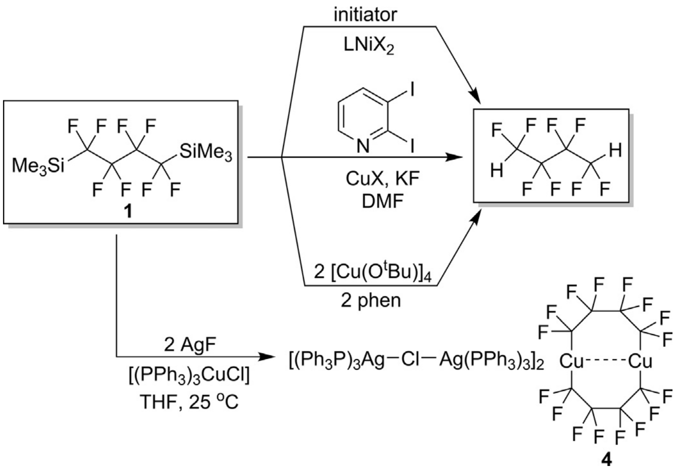


Fig. 1. ORTEP diagram of **1**. One molecule in the asymmetric unit is shown. Selected bond lengths (Å): Si1–C1 1.951(9); Si2–C4 1.931(8); C1–C2 1.528(12); C2–C3 1.539(11); C3–C4 1.536(12). Selected bond angles (°): C2–C1–Si1 118.1(6); C1–C2–C3 118.5(7); C4–C3–C2 118.7(7); C3–C4–Si2 120.4(6).

Thus far, the only clean metal-based transformation involving **1** occurred upon the reaction of $[(PPh_3)_3CuCl]$ in the presence of silver fluoride (Scheme 2). Two new resonances in the ^{19}F NMR spectrum appeared at δ −115.7 and −139.4, which are identical chemical shifts to those found for the recently reported bis-cuprate species $[Cu_2(C_4F_8)_2][Zn(DMF)_6]$.[19] Based on the ^{19}F NMR spectrum and preliminary X-ray data containing a well-ordered cation (Fig. 2) and a disordered anion, this new compound is



Scheme 2. Reactivity of **1** under common perfluoroalkylation conditions.