Unusual C–H Bond Activation and C(sp³)–C(sp³) Bond Formation at an Fe(II) Bis(amide) Carbene Complex

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ABSTRACT: Treatment of $(IMes)Fe(NTMS_2)_2$ with 4 equivalents of methanesulfonyl chloride $(MsCl = MeSO_2Cl)$ resulted in a complex reaction sequence involving substitution of two TMS groups for Ms, followed by the unexpected $C(sp^3)$ –H bond activation of Ms and subsequent $C(sp^3)$ – $C(sp^3)$ bond formation to generate the bimetallic Fe complex, $[IMesH]_2[Cl_2Fe(N(TMS)SO_2(CH_2)_2SO_2N(TMS))_2FeCl_2]$ (1) (IMes = 1,3-bis(2,4,6-trimethylphenyl)-imidazole-2-ylidene; TMS $= SiMe_3)$. Extending this C–H activation/C–C bond forming chemistry to larger alkylsulfonyl chloride chains (i.e. Et, Bu) similarly resulted in C–C coupling, but with decreased chemoselectivity. Detailed mechanistic studies, including using possible intermediate model compounds, were performed in order to elucidate a unifying mechanism for this previously unknown avenue to $C(sp^3)$ – $C(sp^3)$ bond formation.

C-H bond activation is an attractive avenue for the transformation of inexpensive and abundant feedstocks into value-added commodity chemicals. At the industrial level, for example, the DuPont "butox" process catalyzes the partial oxidation of *n*-butane to maleic anhydride via a heterogeneous vanadium phosphorus oxide (VPO) catalyst.1-3 While most research assigned the vanadyl (V=O) centers as the reactive sites for butane C-H bond activation, recent DFT studies suggest that the catalyst support P=O bonds - tethered to neighboring vanadyls may instead be responsible, reacting by a cooperative proton-coupled electron transfer (PCET) mechanism with neighboring high-valent V centers (Scheme 1a).4-6 In order to probe this possible new main-group mediated C-H bond functionalization chemistry, we have recently reported a suite of molecular mono- or multi-metallic VPO model complexes of the general formula, (R_xVⁿ-L)_yP(O)Ar_(3-y) ($R_x = Cp_2$, n = +3, L = O, y = 1, 2, 3, Ar = Ph; R_x = Cp_2 , n = +3, L = O(O)C(C_6H_4), y = 1, 3, Ar = Ph; R_x = $(Ph_2N)_3$, n = +5, L = N, y = 1, Ar = Ph, C_6F_5) $(Cp = \eta^5 - C_5H_5)^{7-1}$ ¹⁰. All of these molecules bear a central M-L-E=O framework where M is the metal redox reservoir (ex. V), L is a resonance linker atom (ex. O, N) or fragment (ex. aryl), and E is the main group center (ex. P). Using the highvalent $(Ph_2N)_3V=N-P(O)Ar_2$ (Ar = Ph or C₆F₅) complexes, we found convincing evidence supporting this proposed PCET pathway using an H-atom donor, as well as an Hatom surrogate in the form of a TMS donor (TMS = Me_3Si) (Scheme 1a).¹⁰ In this report, we outline our attempted expansion into new M-L-E=O frameworks, in particular containing M = Fe and E = S. What we unexpectedly discovered was a reaction sequence involving the spontaneous C(sp³)-H bond activation and C(sp³)-C(sp³) bond formation chemistry outlined in Scheme 1b. Detailed mechanistic studies were performed in an attempt to probe

this unusual reaction mechanism involving this previously unknown and potentially new avenue to $C(sp^3)-C(sp^3)$ bond formation.

Scheme 1. (a) Previous DFT/experimental reports on main-group mediated C-H functionalization (pyz = pyrazine; TMS = $SiMe_3$). (b) This work on C-H bond activation and C-C bond formation using an Fe(II) bis(amide) carbene complex.









RESULTS AND DISCUSSION

In attempting to synthesize our target compound (Scheme 1b), we began by treating the previously reported compound, $(IMes)Fe(NTMS_2)_2$ (IMes = 1,3-*bis*(2,4,6-

trimethylphenyl)-imidazole-2-ylidene),^u with four equivalents of methanesulfonyl chloride (MsCl =



Figure 1. (a) Solid-state molecular structure of 1 revealing $C(sp^3)$ – $C(sp^3)$ bond formation (two [IMesH]+, hydrogen atoms, and all solvent molecules are omitted for clarity). (b) Zero-field ⁵⁷Fe Mössbauer spectrum (90 K) of 1 showing a single quadrupole doublet with an isomer shift (δ) value of 0.37 mm/s and a quadrupole splitting ($|\Delta E_Q|$) value of 0.53 mm/s. (c) Protonolysis of 1 in MeOH and analysis by negative-ion mode ESI-MS showing the C–C coupled fragment 2 in its deprotonated ([2-H]⁻) and desilylated derivatives ([2-TMS]⁻ and [2-2TMS+H]⁻. (d) Partial ¹H-¹³C HSQC NMR spectrum of 3a in D₂O highlighting the CH₂-CH₂ fragment.

MeSO₂Cl). We originally envisioned that TMSCl elimination would furnish our target compound. Mixing these reagents in toluene at room temperature led to darkening of the red solution and subsequent precipitation of a yellow powder after 3 hours of stirring. Isolation of the yellow powder and slow crystallization by diffusion of toluene into a saturated dichloromethane (DCM) solution of the product yielded bright-yellow single-crystals suitable for X-ray diffraction (XRD) studies. The solid-state molecular structure confirmed the composition as the new C(sp³)-C(sp³) coupled product, $[IMesH]_{2}[Cl_{2}Fe(N(TMS)SO_{2}(CH_{2})_{2}SO_{2}N(TMS))_{2}FeCl_{2}]$ (1) (Scheme 1b (R' = H); Figure 1a). The complex featured standard bond metrics, including a C(1)-C(2) bond length of 1.516(9) Å consistent with a C-C single bond.¹² The local geometry around each Fe is distorted octahedral with ligand contributions from two chloride anions and two sulfonamides adopting a κ^2 binding mode through the N and an O atom. Spectroscopic analysis of 1 by zero-field 57Fe Mössbauer spectroscopy (90 K) revealed the presence of a single Fe-containing species with a quadrupole doublet bearing an isomer shift (δ) value of 0.37 mm/s and a quadrupole splitting ($|\Delta E_0|$) value of 0.53 mm/s (Figure 1b). The low isomer shift and narrow quadrupole splitting values are consistent with the pseudo-octahedral, high-spin Fe^{III} complex 1.13 The paramagnetic nature of 1 is further evidenced by a set of four broadened, paramagnetically shifted resonances in the ¹H NMR spectrum (Figure S₁₆). Analysis of 1 by UV-Vis spectroscopy revealed two absorptions centered at 316 nm ($\varepsilon = 1.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and 362 nm (ε = 1.0×10^4 M⁻¹cm⁻¹) which we assign as ligand-to-metal charge transfer (LMCT) bands on the basis of their high extinction coefficients (ϵ) (Figure S7).

We next probed if the organic C–C coupled fragment could be extracted from Fe in 1. We observed clean protonolysis of the Fe–N bonds in 1 upon dissolving it in MeOH. Analysis of the MeOH solution by electron-spray ionization mass spectrometry (ESI-MS) in negative-ion mode revealed major peaks for the free ligand,

(TMS)NHSO₂(CH₂)₂SO₂NH(TMS) (2) in its deprotonated form (2-H)⁻, as well as some of its desilylated derivatives, [2-TMS]⁻ and [2-2TMS+H]⁻ (Figure 1c). Isolation of the fully desilylated bis(sulfonamide) product $H_2NSO_2(CH_2)_2SO_2NH_2$ (3a; Scheme 2) was accomplished by addition of 8 equivalents of HCl (2.0 M in Et₂O) to a solution of 1 in acetonitrile, followed by isolation of the solid precipitate. Analysis of this product by ESI-MS revealed the conversion to 3a (Figure S39). Furthermore, the ¹H NMR spectrum of the residue in D₂O confirmed the formation of a single product with a singlet at 3.70 ppm correlating to a triplet in the ¹³C NMR spectrum at 48.7 ppm as confirmed by 2D ¹H-¹³C HSQC experiments (Figure 1d). Finally, colorless crystals of 3a were grown by slow evaporation of an aqueous solution of the precipitate and unambiguously revealed the intact C-C linkage with identical C(1)-C(2) bond metrics to that of 1. Together, these experiments demonstrate the clean formation of a $C(sp^3)$ - $C(sp^3)$ coupled fragment as the major product (~ 90 %).

Scheme 2. Competing C-C (3a-c), C-Cl (4a-c), and C-S (5a-c) bond forming reactions using different alkylsulfonyl chlorides and following workup.



We next probed if this C–H activation/C–C bond forming chemistry could be extended to longer chains, such as ethyl and butyl. First, treatment of the starting material, (IMes)Fe(NTMS₂)₂, to 4 equivalents of ethylsulfonyl chloride (EsCl) in toluene – analogous to the synthesis of **1** – again led to darkening of the red solution, as well as the subsequent formation of an oil. Multiple attempts to obtain single crystals suitable for XRD experiments failed;

however, analysis of the crude product by zero-field 57Fe Mössbauer spectroscopy (90 K) revealed the presence of a single monopole with δ and $|\Delta E_0|$ values of 0.32 and 0.00 mm/s, respectively, suggesting the presence of a highly symmetric Fe^{III} species dissimilar to 1 (Figure S6). Furthermore, analysis of this crude reaction mixture by positive and negative-ion mode ESI-MS again revealed the formation of the $C(sp^3)$ - $C(sp^3)$ coupled product, **3b**; however, this was in addition to two new, more prominent peaks (Figure S47, S51). Using an acidic workup like the one used in the MsCl reaction resulted in only the ironcontaining species, [FeCl4][IMesH], being isolated. In order to further characterize the product(s) formed, the crude mixture was instead treated to a basic aqueous solution (NaOH) in air in order to hydrolyze the organic fragments and precipitate the iron oxides (rust). These two new products were selectively isolated, yet we were initially unable to interpret their 'H NMR spectra. Fortunately, both were unambiguously identified by single-crystal XRD studies as the products, 4b and 5b (Scheme 2; Figures S32-33). Compound 4b appears to be the result of a double substitution of both TMS groups at N with two EsCl, in addition to a C–Cl bond formation α to the S center. In contrast, we believe **5b** is the product of a side reaction involving a proposed sulfene intermediate (vide infra). The ratio of 4b:5b was approximately 2.5:1 based on ¹H NMR integration (Figure S17). The proposed formation of all of these compounds will be described in the mechanistic section below. Together, however, we estimate a total yield of approximately 60 % for 4b and 5b combined based on NMR assignments and integrations (Figure S17), and trace amounts of **3b** based on ESI-MS (Figure S49). Similar products and distributions were obtained with the use of butylsulfonyl chloride to produce the corresponding products, **3c-5c** (Scheme 2). In contrast to **3b** and **3c**, we reiterate the yield of **3a** was much higher (~ 90 %), likely suggesting an important steric contribution to the fate of these reactions. Lastly, we note that the analogous compounds 4a and 5a (Scheme 2) were observed only by ESI-MS and were not isolated.

In order to gain a better mechanistic picture, we focused on the MsCl reaction and synthesized a series of complexes (6-8) which we initially hypothesized may be relevant to the reaction mechanism (Scheme 3). Compound 6 can be seen as either an Fe^{III} variant of the starting material, (IMes)Fe(NTMS₂)₂, or as a half-fragment of 1 lacking the Ms appendages. The compound was synthesized by addition of [IMesH][Cl] to the known Fe^{III} precursor, Fe(NTMS₂)₂Cl(THF),¹⁴ in benzene. Upon purification, a brick-red powder was isolated in 87 % yield. Single-crystals suitable for XRD studies were grown by vapor diffusion of pentane into a saturated benzene solution of 6 and revealed the expected structure, with the anionic portion isostructural to a previous report (Figure S₃₄).¹⁴ The zerofield 57Fe Mössbauer spectrum of 6 (Figure S1) revealed a broad quadrupole doublet with δ and $|\Delta E_0|$ values of 0.35 and 1.16 mm/s. The UV-Vis spectrum of 6 revealed a prominent band at 420 nm (Figure S8) – similar to the starting material Fe(NTMS₂)₂Cl(THF)¹⁴ at 433 nm - which will be

relevant to the mechanistic study below. All other spectroscopic data for **6** are as expected.

Our original target species, compound 7 (Schemes 1b (R' = H), 3), was next synthesized in a two-step, one-pot protocol involving the addition of Fe(NTMS₂)₂ to two

Scheme 3. C-C bond forming reaction (top) and model complexes 6-8 for mechanistic studies (bottom).



equivalents of N-(trimethylsilyl)methanesulfonamide (MsNH(TMS))¹⁵ resulting in the deprotonation of MsNH(TMS) and formation of TMS₂NH. One equivalent of IMes was subsequently added directly to this reaction mixture. Following isolation and purification, the product was analyzed by zero-field ⁵⁷Fe Mössbauer spectroscopy (90 K) and revealed the presence of a quadrupole doublet with δ and $|\Delta E_Q|$ values of 0.55 and 0.97 mm/s, respectively (Figure S2). Single crystals suitable for XRD studies were grown out of a saturated ether solution at -38 °C. The complex displays distorted trigonal bipyramidal symmetry around Fe (Figure S35). The UV-Vis spectrum of 7 features a broad absorbance at 298 nm ($\epsilon = 7.5 \times 10^2$ M⁻¹cm⁻¹) (Figure S9).

The last model compound synthesized (**8**, Scheme 3), represents the "half-piece" of **1** and was obtained by a similar acid-base approach to the synthesis of **7**. Two equivalents of MsNH(TMS) were added to $Fe(NTMS_2)_2Cl(THF)$ in benzene.¹⁴ Subsequent addition of [IMesH][Cl], and isolation/purification of the product afforded **8** in 89% isolated yield. Single crystals suitable for XRD studies were grown by layering hexamethyldisiloxane (HMDSO) to a saturated THF solution of **8** (Figure 2).



Figure 2. Solid-state molecular structure of **8** representing the "half-fragment" of **1** with identical Fe environments ([IMesH]⁺ and all hydrogen atoms are omitted for clarity).

Interestingly, all relevant bond metrics and angles in 8 are nearly identical to those in 1 (Table S1). (We would like to note that 8 and 1 crystallize in separate space groups, Pbca and P1(bar), respectively, and that 1 does not lie on a center of symmetry and is thus not a product of crystallographic symmetry). The identical Fe environments in 8 and 1 were further confirmed spectroscopically. First, the zero-field ⁵⁷Fe Mössbauer spectrum of **8** (Figure S₃) revealed a single quadrupole doublet with δ and $|\Delta E_Q|$ values of 0.35 and 0.50 mm/s, respectively, virtually identical to the doublet assigned to 1 (0.37 and 0.53 mm/s, respectively; Figure 1b). Second, the UV-Vis spectrum of 8 revealed LMCT bands at 316 and 362 nm, identical to those of 1, but with ε values half as intense, consistent with the reduced metal nuclearity in 8 (Figure S10). Lastly, protonolysis of 8 with MeOH and subsequent analysis by ESI-MS in negative-ion mode revealed a prominent peak at m/z = 166.04, consistent with the ligand fragment [MsN(TMS)]⁻ (Figure S41). No C(sp3)–C(sp3) products, such as in the protonolysis of 1 (Figure 1c), were observed here.

With model compounds 6-8 in hand, we next attempted to establish a unifying mechanism for the C-H activation/C-C bond forming chemistry (3) which would incorporate competing pathways to generate compounds 4 and 5 (Scheme 2). A series of control reactions were first performed. The first involved the reaction of IMes with MsCl in the absence of $Fe(NTMS_2)_2$. Clean conversion to the [IMes][Cl] salt was observed by 'H NMR spectroscopy (Figure S29). The formation of the known cyclic, 4-membered sulfene dimer compound, $(-S(O)_2CH_2-)_2$, is proposed, but was not observed spectroscopically.16 A second control experiment was performed to determine whether IMes was needed in this chemistry. Two equivalents of MsCl was slowly added to a toluene solution of $Fe(NTMS_2)_2$ in the absence of IMes. A dark red product was isolated, purified, and crystallized by slow-cooling a saturated HMDSO solution. The solid-state structure revealed the formation of a bridging, bimetallic, all-ferric siloxide complex of the formula, $((TMS_2N)ClFe)_2(\mu$ -OTMS)₂ (9) (Scheme 4, Figure S₃₆), analogous in many respects to a structure obtained by Holland and co-workers involving the reaction of XFe(NTMS₂) with CO₂ to produce (XFe)₂(μ -OTMS)₂ and

the isocyanate, TMSN=C=O (X = formazanate(1-) ligand).¹⁷ Following an analogous mechanism to theirs, we propose that O extrusion from MsCl leads to siloxide formation and production of the unstable N-silylmethylsulfonimidoyl chloride (TMSN=S(O)MeCl) by-product.¹⁸ Two important observations can be made from this control reaction: 1) One of the four equivalents of MsCl oxidatively delivers chlorine to Fe, and; 2) IMes clearly has an important impact on the reaction outcome (*vide infra*).

Scheme 4. Reaction of Fe(NTMS2)2 with MsCl (2 eq.) to produce 9.



We next turned to UV-Vis spectroscopy in order to garner further mechanistic information on the formation of 1. First, we note that the starting material, (IMes)Fe(NTMS₂)₂, is featureless in the visible range, but possesses a broad absorbance in the near-UV region, starting at 350 nm and extending to the detector limit (275 nm) (Figure 3a, green band). In comparison, as described above, the isolated product 1 exhibits two resonances centered at 316 nm and 362 nm that we assigned as LMCT bands (Figure 3a, black band). With this in mind, we monitored the growth and decay of absorption bands from the reaction of (IMes)Fe(NTMS₂)₂ under saturation kinetics with MsCl (100 eq.) in DCM over time. An initial absorption at 420 nm rapidly grows in within 10 minutes before gradually decaying to two new bands at 316 and 362 nm over the course of 3 hours, consistent with the formation of 1 or 8; however, these experimental conditions should favor the former and not the latter (Figure S₃8) We note that the initial band at 420 nm is analogous to 6 (Scheme 3, Figure S8), or the reported complex Fe(NTMS₂)₂Cl(THF),¹⁴ both of which are Fe^{III} species. The lack of a clean isosbestic point in this reaction is consistent with an expected multi-step pathway involving numerous species. While the growth of 1 revealed no apparent reaction-order dependence, the conversion of 6 (or related Fe^{III} species) to 1 underwent pseudo-first order decay. Furthermore, in monitoring the decay band at 420 nm, a primary kinetic isotope effect (KIE) of 5.51 ± 0.01 was found using deuterium-labelled MsCl-d₃ (Figure 3a, inset).¹⁹



Figure 3. (a) UV-Vis reaction of $(IMes)Fe(NTMS_2)_2$ (green) with MsCl (100 eq.) showing the initial rapid growth of an Fe^{III} species (red), such as 6 (420 nm), followed by its decay to 1 (316, 362 nm, black) over time (grey). Inset is the logarithmic plot of absorbance versus time for the decay of presumed 6 (420 nm) using MsCl (blue) and MsCl- d_3 (grey) revealing a primary kinetic isotope effect of 5.51 ± 0.01. (b) UV-Vis reaction of 6 with MsCl (100 eq.) displaying the formation of 1 (black), but following a zeroth-order kinetic profile in 6.

Scheme 5. Proposed general mechanism for the observed, sterically driven, C–C vs. C–Cl bond forming chemistry starting from $(IMes)Fe(NTMS_2)_2$ and alkylsulfonyl chlorides. A proposed RDS based on kinetic data and featuring a concerted or stepwise PCET reaction sequence is shown in the dashed box. Isolated compounds are drawn in teal and additional details are in gray. A supplemental mechanism accounting for the formation of 5a-c and 9 is outlined in the supporting information.



To further probe the possible intermediacy of **6**, we separately subjected it to MsCl (100 eq.) in DCM and monitored its decay. While analogous decay features producing 1 were again observed, zeroth order reaction kinetics were operational here (Figure 3b). However, we note that 6 contains protonated [IMesH]⁺ in contrast to (IMes)Fe(NTMS₂)₂ which is known to contain free IMes in equilibrium.¹¹ Thus, introducing three equivalents of IMes to the reaction mixture of 6 + MsCl (100 eq.) indeed reintroduced first-order kinetics throughout the reaction process. We were able to extract a pseudo-first order rate constant of $k' = 3.793^{\circ}10^{-3}$ M⁻¹s⁻¹ by independently varying the concentration of MsCl (Figures S14-15). To confirm that 1 - and not the "halfpiece" 8 (Scheme 3) - is formed from the reaction of 6 with MsCl (2 eq.) (Scheme 5, h), protonolysis of the reaction mixture with MeOH and subsequent analysis by ESI-MS revealed major peaks corresponding to the free ligand 2, with no sign of the uncoupled fragment, MsNH(TMS) (Figure S40). Lastly, we investigated the reaction outcome in the absence of any IMes by synthesizing the previously reported Fe^{III} compound, $[Et_4N][Cl_2Fe(NTMS_2)_2]$ (10).²⁰ We found that treatment of this complex with two equivalents of MsCl resulted in a switch in product distribution, this time favouring the α -chlorinated product, **4a** (Scheme 6), and disfavouring the $C(sp^3)$ - $C(sp^3)$ coupled product (2), as observed by ESI-MS following protonolysis in MeOH (Figure S₄₂). Together, these results highlight the importance of IMes in both the rate-determining step (RDS) and in controlling the chemoselectivity of this reaction.

Scheme 6. Reaction of 10 with MsCl (2 eq.) leads to switch in product distribution with α -chlorination product 4a being favoured over C(sp³)—C(sp³) product 3a.



We note that the Fe^{II} compound (7) (Scheme 3) is an unlikely intermediate given that initial TMSCl elimination to produce 7 from (IMes)Fe(NTMS₂)₂, followed by its oxidation to 8 or 1 would preclude the appearance of 6 (or a similar Fe^{III} species) in the UV-Vis spectra (Figure 3). Furthermore, we found that the reaction of 7 with MsCl (2 eq.) vields 8, not 1, as determined by single-crystal XRD studies (Scheme 5, i). In parallel, ESI-MS analysis in negative-ion mode of the crude reaction mixture does not yield peaks for the free ligand 2. Lastly, we note that the "half-piece" 8 is an unlikely intermediate given our unsuccessful attempts at H-atom abstraction (HAA) to yield 1 following radical recombination (Scheme 5, j, Figure S46). Together, these data support a reaction pathway involving initial fast oxidation of Fe^{II} to Fe^{III}, yielding intermediate 6 or a similar Fe^{III} species, followed by a rate-determining C-H functionalization step dependent on IMes and MsCl.

Combining the experimental data above - and focusing first on the MsCl reaction with $(IMes)Fe(NTMS_2)_2$ (R = H, Scheme 5) - we propose a general reaction mechanism involving the initial oxidation of (IMes)Fe(NTMS₂)₂ with MsCl resulting in the formation of an Fe^{III} species consistent with the observed absorption at 420 nm in the UV-Vis spectrum (Scheme 5, path a, Figure 3a). Following this, a proposed RDS (Scheme 5, paths b + c (box)) dependent on both MsCl and IMes, and consistent with the observed KIE (Figure 3a), may involve a concerted or stepwise proton-coupled electron transfer (PCET) reaction resulting in C-H bond activation and the generation of the methylsulfonyl chloride radical which can rapidly dimerize to ClSO₂CH₂CH₂SO₂Cl through C(sp³)-C(sp³) bond formation (Scheme 5, path d). Finally, the reaction of this with proposed Fe^{II} either **6** or the intermediate $[IMesH][ClFe(NTMS_2)_2]$ (Scheme 5, path e) through TMSCl elimination (followed by oxidation for the latter) would lead to the final major product, 1. Based on our experimental observations, this mechanism appears to be sterically driven. With the larger alkylsulfonyl chlorides, a competing reaction involving chlorination of the alkylsulfonyl chloride radical intermediate may result in the formation of products **4b-4c** through a multistep pathway and following hydrolysis (Scheme 5, paths f & g). Lastly, the reactions described previously for compounds 6-8 are also described in Scheme 5 (paths h-j), whereas those outlining the formation of the minor products 5a-c and 9 are described in the supporting information (see section S10).

CONCLUSIONS

To conclude, oxidative C–H functionalization of MsCl using an iron-carbene complex results in a new $C(sp^3)$ – $C(sp^3)$ coupled product **1**. Although heavier alkylsulfonyl chloride substrates similarly result in this type of coupling sequence, a reduction in chemoselectivity for C–C bond formation in favor of C–Cl and C–S bond formation is evidenced using the larger alkylsulfonyl chlorides. This work has demonstrated a potentially new avenue to generating $C(sp^3)$ – $C(sp^3)$ bonds that may be used to build up complex molecular frameworks bearing bis(sulfonamide) functional groups.

ASSOCIATED CONTENT

Supporting Information. Materials and physical methods, synthesis, supplemental figures. This material is available free of charge via the Internet at <u>http://pubs.acs.org</u>.

Accession Codes. CCDC 1954777-1954786 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interests.

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