When SF$_5$ outplays CF$_3$: effects of pentafluorosulfanyl decorated scorpionates on copper†

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Polyfluorinated, electron-withdrawing, and sterically demanding supporting ligands are of significant value in chemistry. Here we report the assembly and use of a bis(pyrazolyl)borate, [Ph$_2$B(3-(SF$_5$)Pz)$_2$]$^-\text{ that combines all such features, and involves underutilized pentafluorosulfanyl substituents. The ethylene and carbonyl chemistry of copper(i) supported by [Ph$_2$B(3-(SF$_5$)Pz)$_2$]$^-$, a comparison to the trifluoromethylated counterparts involving [Ph$_2$B(3-(CF$_3$)Pz)$_2$]$^-$, as well as copper catalyzed cyclopropanation of styrene with ethyl diazoacetate and CF$_3$CH$_2$N$_2$ are presented. The results from cyclopropanation show that SF$_5$ groups dramatically improved the yields and stereoselectivity compared to the CF$_3$.

Introduction

Substituents are the key to modulating the chemical and physical properties of molecules, including those of metal complexes and catalysts. The number of electron-withdrawing substituents that can be utilized for this purpose that are also relatively inert and practical, however, are quite limited. Fluorinated substituents such as the trifluoromethyl (CF$_3$) group are especially useful in this regard as they often drastically alter the properties of a molecule compared to their hydrocarbon counterparts. The pentafluorosulfanyl (SF$_5$) is a noticeably underutilized fluorinated substituent compared to the CF$_3$ group in chemistry. It is, however, gaining increasing attention due to its unique and attractive properties including large size (marginally smaller than a tert-butyl group), strong electron-withdrawing capabilities, high lipophilicity and excellent chemical and thermal stability, and showing great promise in agrochemical, medicinal and materials chemistry applications.

Furthermore, molecules with pentafluorosulfanyl groups are also becoming more accessible via effective and convenient routes. A number of derivatization reactions of SF$_5$-group containing molecules are also known.

The metal complexes featuring SF$_5$ groups are quite limited, although it was a substituent first introduced in 1960. Promising outcomes noted in recent reports suggest that pentafluorosulfanyl moiety merits more closer scrutiny and wider utility. For example, recent work by Mecking and co-workers illustrated the benefits of SF$_5$ over CF$_3$ groups on Ni(II) salicylaldinimato complexes in ethylene polymerization catalysis (to get more linear and higher molecular weight polymers), as well as on tetraphenylborate ions in Ni(II) mediated butadiene polymerizations. In addition, SF$_5$ group has been utilized in luminescent transition metal complexes to minimize the emission features such as blue shifting of the phosphorescent emissions more significantly relatively to CF$_3$ bearing analogs.

Poly(pyrazolyl)borates, commonly referred to as scorpionates, are very valuable class of ligands in coordination chemistry and catalysis, and form complexes with most metals of the periodic table. Here we report the first metal scorpionates decorated with pentafluorosulfanyl groups. In particular, we describe the synthesis of [Ph$_2$B(3-(SF$_5$)Pz)$_2$]$^-$ and the effects of this ligand support on copper(i) as reflected in the structures and bonding of ethylene and CO complexes (which represent two classes of organometallic complexes with significant fundamental and practical significance), and catalytic alkene cyclopropanation, as well as a direct comparison to the related trifluoromethylated analogs (Fig. 1). It is also notable that there...
is only an isolated example of a copper complex involving a 4-
SF5-C6H4-substituted ligand to our knowledge,15 whereas CF3-
bearing ligands with copper are more common and valued in
many applications.11,13

Results and discussion

Synthesis of the SF5-pyrazole

In 1964, Hoover and Coffman reported that a reaction of alkylene
2 with diazomethane in diethyl ether at 0 °C led to the formation
of a mixture of isomeric products 1 and 3 (3:2) (Scheme 1).14 The authors also mentioned that: “these pyrazoles were not
separated.” Therefore, we needed to develop a robust practical
protocol for the SF5-pyrazole 1. After some optimization, we
found that the reaction of alkylene 4 with diazomethane at
−10 °C gave pyrazoline 5 in 85% yield. Oxidation of the latter
with MnO2 followed by crystallization of the resulting material
from hexane gave the needed compound SF5-pyrazole (1) in 38%
yield. This product was obtained in 11 g scale in one run
(Scheme 1).

Synthesis of fluorinated scorpionate ligands and copper–
ethylen complexes

The fluorinated bis(pyrazolyl)borate [Ph2B(3-[SF5]Pz)2]− ligand
possessing SF5 groups at the pyrazolyl ring 3-positions was
prepared by a reaction of SF5-pyrazole (1) with NaBPh4 via

a benzene elimination pathway (Scheme 2, see ESI† section).
This resulting sodium salt was converted to [Ph2B(3-[SF5]Pz)2]Tf
(6) through metathesis using TfOAc, and utilized in the
synthesis of [Ph2B(3-[SF5]Pz)2]Cu(C6H4) (7) by treating with
CuOTf and ethylene (Scheme 2). The related copper–ethylene,
complex [Ph2B(3-[CF3]Pz)2]Cu(C6H4) was also synthesized for
a comparison. They are colorless crystalline solids, and stable to
loss of ethylene in a nitrogen atmosphere at room temperature.
The 19F NMR spectra of the two adducts are very different due
and to the unique square pyramidal arrangement of fluorine atoms in
SF5 moieties vs. trigonal pyramidal array in CF3 groups, leading to
to a doublet and a pentet in the former and a singlet in the
latter.

The ethylene 13C NMR signal in [Ph2B(3-[SF5]Pz)2]Cu(C6H4)
was observed at δ = 86.4 ppm. This resonance in [Ph2B(3-[CF3]
Pz)2]Cu(C6H4) was observed at δ 82.7 ppm, which is an even
larger upfield shift from the free C6H4 (δ 123.1 ppm) signal.
Larger upfield shift of the metal bound ethylene 13C resonance
from the free C6H4 (δ 123.1 ppm) signal has been attributed to
the increased shielding resulting from metal-to-ethylene π-
back-donation.15 Thus [Ph2B(3-[SF5]Pz)2]Cu(C6H4), with a smaller upfield shift points to relatively lower Cu → ethylene
π-backbonding. This is reasonable considering the presence of
more electron withdrawing SF5 groups (with an estimated
electron negativity of 3.65 vs. 3.36, and Hammett substituent
constant σm of 0.61 vs. 0.43 for SF5 vs. CF3).2,16 on the scorpionate
ligand backbone of this copper complex. For comparison, three
coordinate [t-Bu2P(NSiMe3)2]Cu(C6H4) with a more strongly
backbonding copper site displays its ethylene carbon shift at
δ 73.0 ppm.17 The 13C NMR data are particularly useful for such
bonding analysis since they are less affected by the ring current

effects.

The ethylene protons of [Ph2B(3-[R]Pz)2]Cu(C6H4) (R = −SF5,
−CF3) in the 1H NMR spectrum appear at δ 3.72 and 3.69 ppm,
respectively. These protons are most likely affected by the ring
curvature of flanking phenyl groups sitting over ethylene moieties (see molecular structures below). The presence of additional ethylene in CDCl3 solutions at room temperature leads to
separate broad signals of free and coordinated ethylene in
[Ph2B(3-[CF3]Pz)2]Cu(C6H4) whereas these signals remain sharp for
the −SF5 analog 7, suggesting a quite rapid olefin exchange only
in the former at room temperature on the NMR time scale.

X-ray crystal structures of Cu–ethylene complexes

Molecular structure of [Ph2B(3-[R]Pz)2]Cu(C6H4) (R = SF5, CF3)
were unambiguously established by single-crystal X-ray

Scheme 1 Synthesis of SF5-pyrazole 1.

Scheme 2 Synthesis of [Ph2B(3-[SF5]Pz)2]Cu(C6H4).
We have also investigated alkene–copper(i) bonding of [Ph₂B(3-(SF₅)Pz)₂]Cu(C₂H₄), [Ph₂B(3-(CF₃)Pz)₂]Cu(C₂H₄), and the hypothetical [Ph₂B(3-(CH₃)Pz)₂]Cu(C₂H₄) via density functional calculations. The calculated interaction energy (ΔEint) between the ethylene and Cu(i) center remains similar, ranging from -44.9, -45.9, to -45.2 kcal mol⁻¹ (Table 1), respectively, which is further dissected in different contributions within the Ziegler–Rauk energy decomposition analysis (EDA).¹ It shows that these interactions are primarily electrostatic in nature for all three [Ph₂B(3-(R)Pz)₂]Cu(C₂H₄) complexes as evident from ΔEelstat of about ~60%, with the remainder consists of ~36% orbital contributions (ΔEorb) and ~4% dispersion-type interactions (ΔEdisp). The ΔEorb of [Ph₂B(3-(SF₅)Pz)₂]Cu(C₂H₄) composed of σ-donation and π-backdonation ascribed to the π₁-C₂H₄ → Cu and π₂-C₂H₄ ← Cu (Fig. S43, ESI†) in a 29.9% and 54.9% contribution, respectively, which is similar in trend but shows a gradual decrease and an increase in the two components going from –SF₅ to the –CF₃ and –CH₃ analogs, culminating in 24.5% and 63.7%, σ/π-contributions in the most electron rich scorpionate ligand analog [Ph₂B(3-(CH₃)Pz)₂]Cu(C₂H₄). These interactions cause a more red-shifted ν(C=C) as evident from the computed values of 1516.3, 1513.5 and 1509.3 cm⁻¹, for [Ph₂B(3-(R)Pz)₂]Cu(C₂H₄) (R = –SF₅, –CF₃, –CH₃, respectively). These numbers follow the order of Hammett substituent constant σₚ/[σₚ] [0.61/0.68, 0.43/0.54, and -0.07/-0.17 for –SF₅, –CF₃, –CH₃, respectively]²,³ and are inversely related to the π₁-C₂H₄ ← Cu backbonding contribution (Table 1). This trend is also consistent with computed proton affinities of the [Ph₂B(3-(R)Pz)₂]⁻ ligands and therefore, the donor features of the scorpionate nitrogen sites; see ESI Table S17†, and indicate that [Ph₂B(3-(SF₅)Pz)₂]Cu(C₂H₄) features the most weakly donating scorpionate and least backbonding copper site in this series.

Olefin displacement leading to Cu-carbonyl complexes

Some reactivities and catalytic features of [Ph₂B(3-(SF₅)Pz)₂]Cu(C₂H₄), [Ph₂B(3-(CF₃)Pz)₂]Cu(C₂H₄) have also been

Table 1. Energy decomposition analyses for the C₂H₄–Cu interaction for different [Ph₂B(3-(R)Pz)₂]Cu(C₂H₄) complexes, with R = –SF₅, –CF₃, and –CH₃. Values in kcal mol⁻¹. In addition, π-backbonding and σ-donation components are given as π₁-C₂H₄ ← Cu and π₂-C₂H₄ ← Cu, respectively. Calculated ν(C=C) (in cm⁻¹) values are also given

| Parameter | [Ph₂B(3-(SF₅)Pz)₂]Cu(C₂H₄) | [Ph₂B(3-(CF₃)Pz)₂]Cu(C₂H₄) | [Ph₂B(3-(CH₃)Pz)₂]Cu(C₂H₄) |
|-----------|-----------------------------|-----------------------------|-----------------------------|
| ΔEelstat  | -44.9                       | -45.9                       | -45.2                       |
| ΔEbvol    | 114.0                       | 112.5                       | 125.4                       |
| ΔEdisp    | -6.5 4.1%                   | -5.6 3.5%                   | -5.3 3.1%                   |
| ΔEelstat  | -95.2 59.9%                 | -95.0 59.9%                 | -102.1 59.9%                |
| ΔEorb     | -57.2 36.0%                 | -57.9 36.6%                 | -63.2 37.1%                 |
| π₁-C₂H₄ → Cu | -17.1 29.9%              | -16.5 28.5%                 | -15.5 24.5%                 |
| π₂-C₂H₄ ← Cu | -31.4 54.9%              | -33.5 57.9%                 | -40.2 63.7%                 |
| ΔEππ       | -8.7                        | -7.8                        | -7.5                        |
| ν(C=C) calc. | 1516.3                  | 1513.5                      | 1509.3                      |

α Percentage contribution to the total attractive interactions ΔEelstat + ΔEorb + ΔEdisp. β Percentage contribution to the total orbital interactions ΔEππ.
investigated. Upon treatment with CO in CH$_2$Cl$_2$, both adducts afford the corresponding copper carbonyl complexes. They do not lose CO under reduced pressure. The CO stretching frequencies of [Ph$_2$B(3-(SF$_5$)P$_2$)$_2$]Cu(CO) and [Ph$_2$B(3-(CF$_3$)P$_2$)$_2$]Cu(CO) were observed at 2121 and 2117 cm$^{-1}$, respectively. For comparison, the ν(CO) for the highly fluorinated [H$_2$B(3,5-(CF$_3$)$_2$P$_2$)]Cu(CO)$^{29}$ and relatively electron rich [(Ph$_3$B)(CH$_3$)$_2$]Cu(CO)$^{29}$ appear at 2127 and 2092 cm$^{-1}$, respectively. These data indicate that [Ph$_2$B(3-(SF$_5$)P$_2$)$_2$]Cu(CO) has a notably Lewis acidic copper site, and a relatively weakly donating supporting scorpionate, consistent with the observed carbon chemical shifts and DFT analysis of the corresponding ethylene complex. DFT calculations show that the Cu–CO interaction (ESI†) is slightly less favorable than Cu–C$_2$H$_4$ (Table 1) in the corresponding [Ph$_2$B(3-($R$)P$_2$)$_2$]Cu(CO) (Δ$E_{\text{int}}$ = −39.9 (R = SF$_5$), −39.8 (R = CF$_3$), and −40.9 kcal mol$^{-1}$ (for hypothetical R = CH$_3$)). The thermochemical parameters for the observed C$_2$H$_4$ → CO replacement in 7 and its –CF$_3$ counterpart were also estimated computationally, which show that the free-energy change at room temperature (Δ$G^{298}$ K) for these reactions are very small at +1.30 and +0.59 kcal mol$^{-1}$, respectively. They are essentially thermo-neutral processes. Indeed, it is possible to treat CHCl$_3$ solutions of [Ph$_2$B(3-(SF$_5$)P$_2$)$_2$]Cu(CO) and [Ph$_2$B(3-(CF$_3$)P$_2$)$_2$]Cu(CO) with ethylene at room temperature to regenerate the corresponding ethylene complexes. The Cu–CO bonding features of [Ph$_2$B(3-(R)P$_2$)$_2$]Cu(CO) were also investigated using DFT and found to vary systematically along the R = SF$_5$, –CF$_3$, and –CH$_3$ series, with the lowest 2π* ← Cu back-bonding observed for [Ph$_2$B(3-(SF$_5$)P$_2$)$_2$]Cu(CO), leading to the calculated ν(CO) of 2110, 2099, and 2080 cm$^{-1}$, respectively (ESI†).

Molecular structures of [Ph$_2$B(3-(SF$_5$)P$_2$)$_2$]Cu(CO), [Ph$_2$B(3-(CF$_3$)P$_2$)$_2$]Cu(CO) are illustrated in Fig. 4. There are two chemically identical molecules of [Ph$_2$B(3-(SF$_5$)P$_2$)$_2$]Cu(CO) in its asymmetric unit. Selected bond angles and distances are presented in Table S3 (ESI†). The Cu–CO moieties are essentially linear. The scorpionate coordinates to the metal ion in κ$^2$ fashion and adopts a boat configuration. One of the phenyl groups on boron sits above the copper center. The metal to ipso-carbon distances are 2.58 and 2.78 Å in [Ph$_2$B(3-(R)P$_2$)$_2$]Cu(C$_2$H$_4$) (R = –SF$_5$, –CF$_3$), respectively. These separations are within the sum of van der Waals radii of Cu and C (3.10 Å). However, these contacts do not appear to be significant enough to distort the coordination geometry at the metal center because these molecules feature trigonal planar metal sites as evident from the sum of angles at the metal center (~360°). Furthermore, the ν(CO) values suggest that the copper sites remain quite Lewis acidic despite the close approach of the phenyl groups. Note that three-coordinate, trigonal planar copper carbonyls are very limited.$^{22}$

Analysis of the topographic steric maps of the two metal complexes using SambVca$^*$ and the X-ray crystallographic data indicate percent buried volumes (%$\text{V}_{\text{bur}}$) of 72.8% and 66.3% for [Ph$_2$B(3-(SF$_5$)P$_2$)$_2$]Cu(CO) and [Ph$_2$B(3-(CF$_3$)P$_2$)$_2$]Cu(CO), respectively clearly indicating more protected copper sites in the former as a result of having sterically more demanding SF$_5$ groups at the periphery of the coordination pocket (Fig. S41, ESI†). These percent buried volume values are larger than those observed for the related ethylene analogs (described above), indicating the adaptability of the scorpionate to accommodate organometallic fragments of different sizes.

**Catalytic activity of copper-complexes**

Finally, we have also investigated the catalytic potential of [Ph$_2$B(3-(R)P$_2$)$_2$]Cu(C$_2$H$_4$) (R = –SF$_5$, –CF$_3$) in cyclopropanation *via* a carbene transfer process. It was found that on reaction of styrene with ethyl diazoacetate (EDA), both copper(I) complexes serve as carbene transfer agents providing the expected cyclopropane as a diastereomeric mixture (Scheme 2). However, [Ph$_2$B(3-(SF$_5$)P$_2$)$_2$]Cu(C$_2$H$_4$) gave dramatically higher cyclopropane product yields (99% vs. 62%) and greater *cis*-selectivity (3 : 2 vs. 1 : 1) compared to the –CF$_3$ substituted analog (Scheme 2).

These results are consistent with the previous reports by Perez and co-workers involving tris(pyrrozyl)boratocopper complexes and EDA, which indicate that the higher *cis*-selectivities are associated with bulkier supporting ligands.$^{23}$ Interestingly, when CF$_3$CH$_2$N$_2$ was used as the carbene source,$^{24}$ [Ph$_2$B(3-(SF$_5$)P$_2$)$_2$]Cu(C$_2$H$_4$) again gave notably higher product yields than the [Ph$_2$B(3-(CF$_3$)P$_2$)$_2$]Cu(C$_2$H$_4$) catalyzed process, but this time, the *trans*-isomer was the major product. It is also
known that the cis-isomer is the kinetic product while the trans-isomer is the thermodynamically favored product. Therefore, it is possible that the greater steric bulk of the diazo reagent CF₂CHN₂ (compared to EDA) favors the latter, causing this interesting reversal in diastereoselectivity. Indeed, Doyle et al. has observed high trans-selective cyclopropanations in rhodium chemistry with bulky diazo reagents (Scheme 3).

Conclusions

Overall, we have described the preparation and characterization of the first pentfluorosulfonyl decorated scorpionate [Ph₂B(3-(SF₅)Pz)₂]− and some of its copper chemistry, as well as a new, regioselective route to SF₅-pyrazole. The [Ph₂B(3-(SF₅)Pz)₂]− is a more sterically demanding and weakly donating ligand compared to the [Ph₂B(3-(CF₃)Pz)₂]−, as evident from the copper ethylene and carbonyl chemistry and computational analysis. Moreover, the [Ph₂B(3-(SF₅)Pz)₂]Cu(C₂H₄) (7) complex displays significantly better efficacy in cyclopropanation of styrene with EDA and CF₂CHN₂ compared to that of [Ph₂B(3-(CF₃)Pz)₂]Cu(C₂H₄). Fluorinated ligands are important as they often provide metal complexes with certain beneficial features relative to the non-fluorinated, hydrocarbon group bearing ligands. Given the common appearance of CF₃-ligands in various areas of chemistry, we believe that with this work, the SF₅-analogues will also become popular. Further studies on metal complexes supported by SF₅ containing ligands and practical approaches to other SF₅-heterocycles are currently underway.

Data availability

All data associated with this article can be found in the ESI.

Author contributions

Conceptualization: HVRD, PM; investigation: AN-P, AM-C, AB; writing and validation: AN-P, AM-C, AB, PM, HVRD; project administration: HVRD.

Conflicts of interest

There are no conflicts to declare.

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