Journal of Fluorine Chemistry 140 (2012) 112–115

Contents lists available at SciVerse ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Short Communication

Synthesis and structure of a bis-trifluoromethylthiolate complex of nickel

Cheng-Pan Zhang [a], William W. Brennessel [b], David A. Vicic [a,*]

[a] Department of Chemistry, University of Hawaii, 2545 McCarthy Mall, Honolulu, HI 96822, USA
[b] The X-ray Crystallographic Facility, Department of Chemistry, University of Rochester, Rochester, NY 14627, USA

ARTICLE INFO

Article history:
Received 16 April 2012
Received in revised form 27 April 2012
Accepted 1 May 2012
Available online 8 May 2012

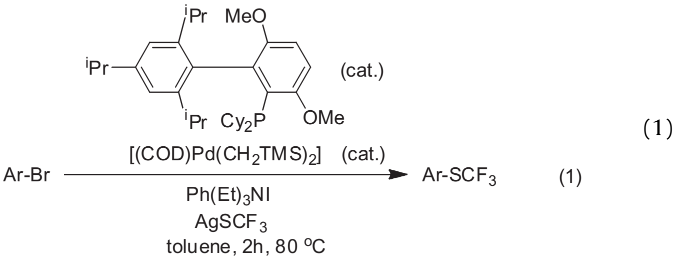
Keywords:
Sulfur
Nickel
Organometallic
Fluorine

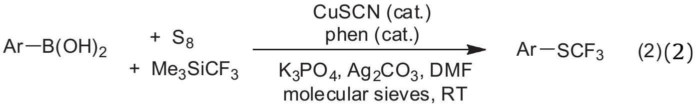
ABSTRACT

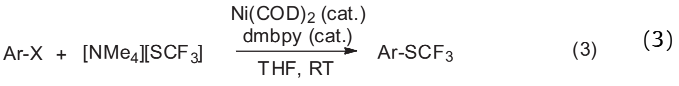
Reaction of [(dippe)NiI$_2$] (dippe = 1,2-bis(diisopropylphosphino)ethane) with excess [NMe$_4$][SCF$_3$] led to the formation of [(dippe)Ni(SCF$_3$)$_2$] (**1**) in 92% isolated yield. Complex **1** has been structurally characterized, and the data provides the first experimentally determined bond parameters of a nickel–trifluoromethylthiolate complex. The molecule lies on a two-fold axis, with nickel-phosphorus bonds of 2.1828(4) Å and nickel-sulfur bonds of 2.2395(4) Å. Density functional theory (DFT) calculations predict that the highest occupied molecular orbital (HOMO) is sulfur-centered and the lowest unoccupied molecular orbital (LUMO) is nickel-centered.

1. Introduction

The SCF$_3$ functional group has become increasingly important in the agrochemical and pharmaceutical fields.[1] Its extremely high Hansch lipophilicity parameter ($\pi = 1.44$)[2] makes the SCF$_3$ group appealing for the design of new molecules capable of crossing lipid membranes. Although a variety of novel methods exist to incorporate an SCF$_3$ group into organic substrates, [1a] only recently have metal-catalyzed SCF$_3$-coupling processes begun to emerge. Three recent breakthroughs in metal-catalyzed trifluoromethylthiolation are shown in Eqs. (1)–(3). A palladium complex bearing the bulky Brettphos ligand was found to mediate the cross-coupling of aryl bromides with AgSCF$_3$ as described in Eq. (1) [1c]. The employment of the silver trifluoromethylthiolate reagent was necessitated by the fact that the cross-couplings occur at elevated temperatures. Aryl chlorides were not amenable to the conditions described in Eq. (1). Since aryl chlorides can be catalytically converted to aryl boronic acids [3], the copper-catalyzed oxidative trifluoromethylthiolation reaction described in Eq. (2) offers a nice alternative approach to the formation of aryl trifluoromethyl sulfides [1d]. However, this approach also employs the use of stoichiometric amounts of silver salts. The use of a simple nickel bipyridine system described in Eq. (3) (dmbpy = 4,4′-dimethoxybipyridine) allows for the cross-coupling of aryl iodides and bromides to occur under room temperature conditions with the convenient [NMe$_4$][SCF$_3$] reagent [4] and avoids the use of silver salts altogether [1b].







Because of the promising reactivity of the nickel system, we became interested in obtaining experimental structural parameters of a nickel–SCF$_3$ bond. Attempts to prepare (bipyridine)Ni trifluoromethylthiolate complexes related to the catalytically active species in Eq. (3) have thus far not yielded any successful results, so we turned our attention to other ligands which might be able to support trifluoromethylthiolate bonding. One ligand that

---

[*] Corresponding author.
E-mail address: vicic@hawaii.edu (D.A. Vicic).

0022-1139/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jfluchem.2012.05.003

we targeted was dippe. Many studies have focused on using the [(dippe)Ni] fragment as active desulfurization agents, so many structurally characterized [(dippe)Ni] compounds exist with nickel–sulfur bonds [5]. Since this collection of structures is very attractive for comparative purposes, efforts turned toward preparing [(dippe)Ni(SCF_3)$_2$] (**1**).

2. Results and discussion

It was found that reaction of [(dippe)NiI$_2$] [6] with excess [NMe$_4$][SCF$_3$] led to the formation of **1** in 92% isolated yield. The ^{19}F NMR spectrum (CD_2Cl_2) of **1** displays a singlet at δ −19.9, indicating the presence of equivalent SCF_3 groups. The $^{13}C\{^1H\}$ NMR spectrum (CD_2Cl_2) clearly showed the presence of the SCF_3 carbon atom as a quartet at δ 135.0 with $J_{C-F} = 304$ Hz. X-ray quality crystals of **1** could be grown by layering a THF solution of **1** with pentane, and the X-ray structure (Fig. 1) is consistent with the symmetric geometry observed in solution phase. Details of the data collection are summarized in Table 1. The molecule lies along a crystallographic two-fold axis which includes the nickel atom. The twist angle between P-Ni-P and S-Ni-S planes is 11.69(2) degrees. Interestingly, the nickel-phosphorus and nickel-sulfur bond distances are both slightly longer than those for the known [(dippe)Ni($S_2C_2H_4$)] (**2**) and [(dippe)Ni(SAr)$_2$)] (**3**, Table 2).

DFT calculations were performed in order to determine the optimized bond lengths and angles for **1** in the gas phase, and the results are provided in Table 2. Calculations predict a slightly more elongated nickel–phosphorus bond and slightly contracted nickel–sulfur bonds. The HOMO, HOMO-1, and LUMO of **1** were also evaluated computationally, and the results are depicted in Fig. 2. The largest molecular orbital coefficients (Mulliken) for both the HOMO and HOMO-1 of **1** were sulfur-centered, while those for the LUMO were dominated by the nickel atom. The HOMO and HOMO-1 contributions came largely from the two sulfur's p_x and p_y orbitals, respectively. The largest molecular orbital coefficients (Mulliken) for the LUMO of **1** were dominated by the nickel d_{yz} orbital with slight contributions from the d_{xy}. Charge distributions (Fig. 2) show that the sulfur atoms bear a negative charge that is not as large in magnitude as those on the fluorine. This distribution is in contrast to that recently reported for [(SIPr)Cu(OCF_3)] (SIPr = *N*,*N*′-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene) [8], in which the oxygen atom bore the highest charge of −0.87e while that of the fluorines were calculated to be −0.39, −0.38, and −0.41e. The carbon atom of the SCF_3 group in **1** was also found to have a less positive charge (0.93e) than that in [(SIPr)Cu(OCF_3)] (1.32e).

Table 1
Crystal data and refinement parameters for (dippe)Ni(SCF_3)$_2$ [7].

Compound	1
Chemical formula	$C_{16}H_{32}F_6NiP_2S_2$
Formula weight	523.19
Crystal dimensions (mm)	0.20 × 0.18 × 0.12
Color, habit	Orange, block
Crystal system	Monoclinic
Temperature	100.0(5) K
Wavelength (Å)	0.71070
Space group (*Z*)	C2/c, 4
a (Å)	9.1592(9)
b (Å)	17.3494(16)
c, (Å)	14.4664(14)
α (°)	90
β (°)	94.703(2)
γ (°)	90
vol, (Å^3)	2291.1(4)
ρ_{calc} (mg/m^3)	1.517
R indices [$I > 2$ sigma(I)]	$R_1 = 0.0575$ $wR_2 = 0.1538$
R indices [all data]	$R_1 = 0.0728$ $wR_2 = 0.1652$
Goodness of fit	1.080
θ Range (°)	2.35–37.78
Number of data collected	33,333
Number of unique data	6103
R_{int}	0.0650
Absorption correction	Multi-scan
Data/restraints/parameters	6103/0/127
Goodness-of-fit on F^2	1.043
Final *R* indices [$I > 2$sigma (I)]	$R_1 = 0.0392$ $wR_2 = 0.0843$
R indices (All data)	$R_1 = 0.0392$ $wR_2 = 0.0843$

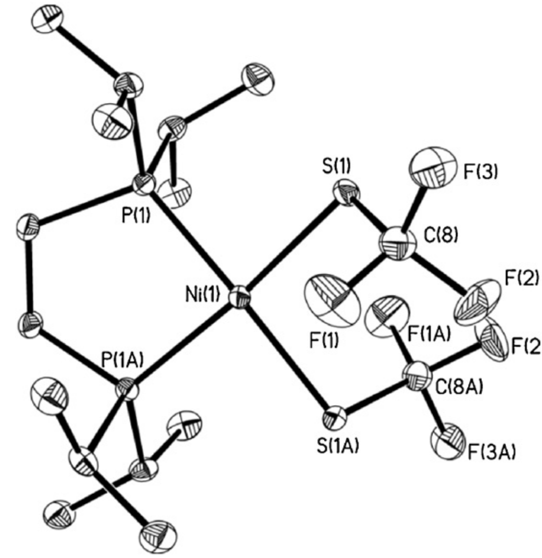
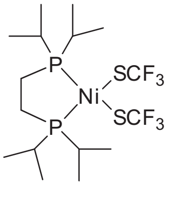
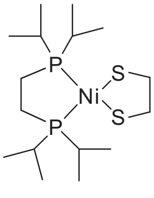


Fig. 1. ORTEP diagram of [(dippe)Ni(SCF_3)$_2$] (**1**). Ellipsoids shown at the 50% level. Hydrogen atoms are removed for clarity. Selected bond lengths (Å): F1-C8 1.3443(19); F2-C8 1.3447(19); F3-C8 1.3576(17). Selected bond angles (°): F(1)-C(8)-F(2) 105.09(13); F(1)-C(8)-F(3) 105.64(13); F(2)-C(8)-F(3) 104.58(12); F(1)-C(8)-S(1) 114.73(11); F(2)-C(8)-S(1) 115.63(11); F(3)-C(8)-S(1) 110.23(10).

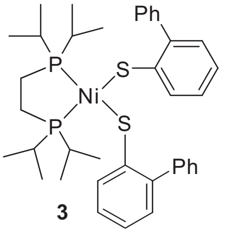
Table 2
Experimental and calculated bond lengths (Å) and angles (°) in selected compounds.



1



2



3

Bond length or angle	Complex 1 expt.	Complex 1 calc.	Complex 2 expt. [5a]	Complex 3 expt. [5f]
Ni–P1	2.1828(4)	2.223	2.156(2)	2.1728(7)
Ni–P2	2.1828(4)	2.223	2.154(2)	2.1831(7)
Ni–S1	2.2395(4)	2.272	2.179(2)	2.2298(7)
Ni–S2	2.2395(4)	2.273	2.181(2)	2.2252(7)
C1–S1	1.7685(15)	1.800	1.820(7)	1.762(3)
C2–S2	1.7685(15)	1.800	1.810(8)	1.775(2)
S1–Ni–S2	96.66(2)	95.56	93.41(8)	98.16(3)
P1–Ni–P2	87.87(2)	88.39	89.17(7)	88.60(3)
P1–Ni–S1	88.354(14)	88.57	90.54(8)	86.06(3)
P1–Ni–S2	170.508(13)	171.33	165.19(8)	174.84(3)
P2–Ni–S1	170.508(13)	171.33	164.80(9)	172.58(3)
P2–Ni–S2	88.3354(14)	88.57	90.70(8)	87.46(3)

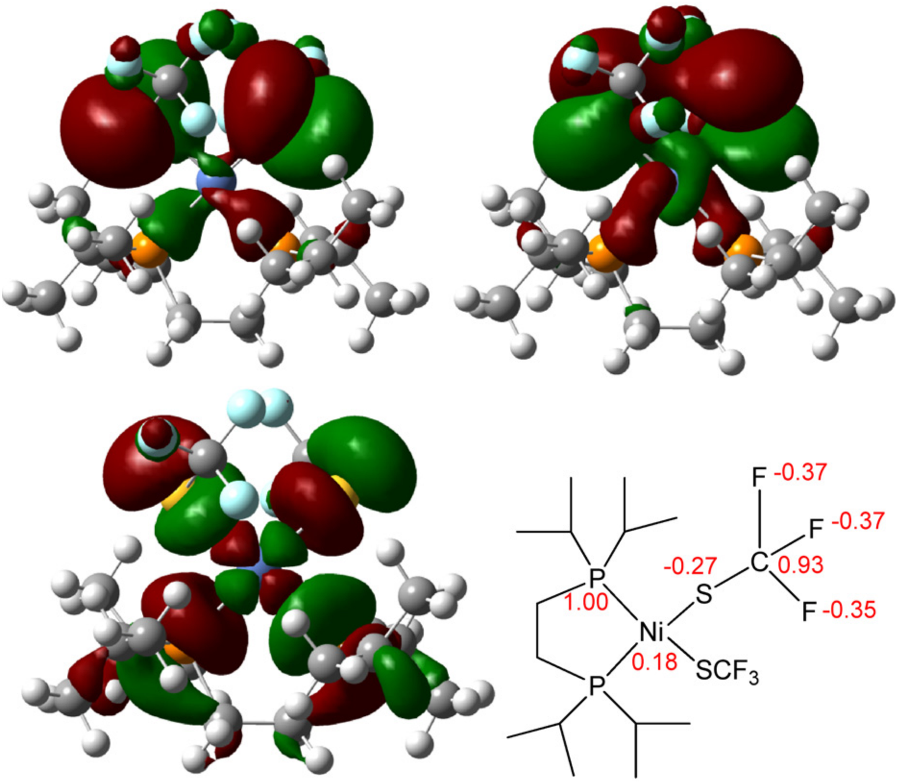


Fig. 2. Top left: calculated HOMO (−5.38 eV). Top right: Calculated HOMO-1 (−5.41 eV). Bottom left: calculated LUMO (−1.58 eV). Bottom right: selected calculated natural atomic charges in **1**.

3. Conclusions

The first stable trifluoromethylthiolate complex of nickel has been synthesized, structurally characterized, and evaluated computationally. With this new complex in hand, it is hoped that explorations of stoichiometric reactions with organic substrates will ultimately lead to better methods development and a better understanding of how to manipulate the trifluoromethylthiolate group.

4. Experimental procedures

4.1. General considerations

All manipulations were performed using standard Schlenk and high vacuum techniques or in a nitrogen filled glovebox. Solvents were distilled from Na/benzophenone or CaH_2. ^1H NMR spectra were recorded at ambient temperature on a Varian Oxford 300 MHz spectrometer and referenced to residual proton solvent signals. $^{13}C\{^1H\}$ NMR spectra were recorded on the Varian Oxford spectrometers operating 125 MHz and referenced to solvent signals. ^{19}F spectra were recorded on the Varian Oxford spectrometer operating at 282 MHz. $[NMe_4][SCF_3]$ was prepared according to a previously published procedure.

4.1.1. Preparation of complex 1

In a glovebox, (dippe)NiI_2 (57 mg, 0.1 mmol) and $[NMe_4][SCF_3]$ (59 mg, 90%, 0.3 mmol) were dissolved in dry THF (4 mL). The mixture was stirred at room temperature for 2 days, then filtered through a glass frit. Pentane (15 mL) was gently added into the filtrate. The suspension was kept in a freezer (−30 °C) until dark brown–red crystals were formed (48 mg, 92% yield). ^1H NMR (300 MHz, CD_2Cl_2): δ 2.53 (m, 4H), 1.72 (d, J = 12.3 Hz, 4H), 1.41 (dd, J = 16.7 Hz, J = 7.3 Hz, 12H), 1.27 (dd, J = 13.6 Hz, J = 7.0 Hz, 12H). ^{19}F NMR (282 MHz, CD_2Cl_2): δ −19.9 (s, 6F). ^{31}P NMR (121 MHz, CD_2Cl_2): δ 85.1 (m). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 135.0 (q, J = 304 Hz, SCF_3), 26.3 (t, J = 13.4 Hz), 21.0 (t, J = 19.1 Hz), 20.3, 18.5. Anal. Calcd (found) for $C_{16}H_{32}F_6NiP_2S_2$: C, 36.73 (36.79); H, 6.16 (5.99).

4.2. Computational details

All of the calculations were performed using the Gaussian09W package [9]. Unrestricted quantum calculations were performed using the B3LYP exchange-correlation functional [10]. The nickel atom was represented with the m631-g* basis set [11] and the remaining atoms were represented with 6-31g(d,p) basis set stored internally in the Gaussian program. The geometry optimizations were performed without any symmetry constraints, and the local minima were checked by frequency calculations.

Acknowledgement

D.A.V. thanks the Office of Basic Energy Sciences of the U.S. Department of Energy (DE-FG02-07ER15885).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2012.05.003.

References

[1] (a) V.N. Boiko, Beilstein, J. Org. Chem. 6 (2010) 880–921;
(b) C.-P. Zhang, D.A. Vicic, J. Am. Chem. Soc. 134 (2012) 183–185;
(c) G. Teverovskiy, D.S. Surry, S.L. Buchwald, Angew. Chem. Int. Ed. 50 (2011) 7312–7314;
(d) C. Chen, Y. Xie, L. Chu, R.-W. Wang, X. Zhang, F.-L. Qing, Angew. Chem. Int. Ed. 51 (2012) 2492–2495.

[2] C. Hansch, A. Leo, S.H. Unger, K.H. Kim, D. Nikaitani, E.J. Lien, J Med. Chem. 16 (1973) 1207–1216.

[3] G.A. Molander, S.L.J. Trice, S.D. Dreher, J. Am. Chem. Soc. 132 (2010) 17701–17703.

[4] W. Tyrra, D. Naumann, B. Hoge, Y.L. Yagupolskii, J. Fluorine Chem. 119 (2003) 101–107.

[5] (a) S.S. Oster, R.J. Lachicotte, W.D. Jones, Inorg. Chim. Acta 330 (2002) 118–127;
(b) D.A. Vicic, W.D. Jones, J. Am. Chem. Soc. 121 (1999) 7606–7617;
(c) D.A. Vicic, W.D. Jones, J. Am. Chem. Soc. 121 (1999) 4070–4071;
(d) D.A. Vicic, W.D. Jones, Organometallics 17 (1998) 3411–3413;
(e) J. Campora, I. Matas, P. Palma, E. Alvarez, C. Graiff, A. Tiripicchio, Organometallics 26 (2007) 3840–3849;
(f) J. Torres-Nieto, W.W. Brennessel, W.D. Jones, J.J. García, J. Am. Chem. Soc. 131 (2009) 4120–4126;
(g) D.A. Vicic, W.D. Jones, J. Am. Chem. Soc. 119 (1997) 10855–10856;
(h) M.J. Tenorio, M.C. Puerta, P. Valerga, J. Chem. Soc. Dalton Trans. (1996) 1935–1939;
(i) M.R. Grochowski, T. Li, W.W. Brennessel, W.D. Jones, J. Am. Chem. Soc. 132 (2010) 12412–12421;
(j) L. Gonzalez-Sebastian, M. Flores-Alamo, J.J. Garcia, Dalton Trans. 40 (2011) 9116–9122.

[6] G.G. Dubinina, W.W. Brennessel, J.L. Miller, D.A. Vicic, Organometallics 27 (2008) 3933–3938.

[7] Crystallographic data (excluding structure factors) for compound **1** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 861455. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 1223 336 033; deposit@ccdc.cam.ac.uk].

[8] C.-P. Zhang, D.A. Vicic, Organometallics, http://dx.doi.org/10.1021/om3002747.

[9] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. Montgomery, J.A., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N.J. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09 for Windows, Rev. C.01, 2009.

[10] (a) A.D. Becke, J. Chem. Phys. 98 (1993) 5648–5652;
(b) C. Lee, W. Yang, R.G. Parr, Phys. Rev. B: Condens. Matter. 37 (1988) 785–789.

[11] A.V. Mitin, J. Baker, P. Pulay, J Chem. Phys. 118 (2003) 7775–7782.