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Short Note

4,4′-Di-*tert*-butyl-2,2′-bipyridinium Trifluoromethanesulfonate

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Abstract: 4,4′-Di-*tert*-butyl-2,2′-bipyridinium trifluoromethanesulfonate was synthesized by stirring 4,4′-Di-*tert*-butyl-2,2′-bipyridine with scandium(III) trifluoromethanesulfonate in acetonitrile, followed by precipitation with diethyl ether. The structure of the new compound was characterized by FT-IR, ^{1}H, ^{13}C{^{1}H} and ^{19}F{^{1}H} NMR spectroscopy and CHN elemental analysis. This is a safe and simple method to obtain mono-protonated bipyridinium trifluoromethanesulfonate without the direct use of trifluoromethanesulfonic acid.

Keywords: 2,2′-bipyridinium; bidentate nitrogen ligand; scandium(III) trifluoromethanesulfonate

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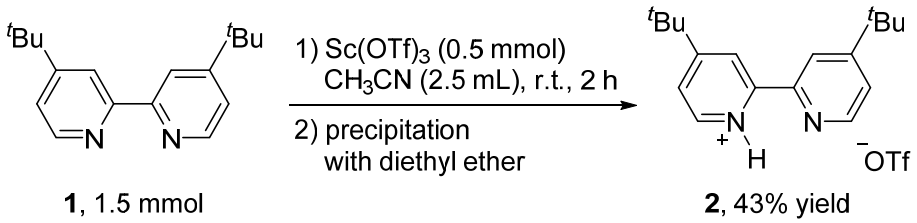
1. Introduction

Protonated pyridinium salts are widely used in synthetic organic reactions (e.g., oxidation reactions [1], Brønsted acid-catalyzed reactions [2–4], and photochemical reactions [5]), host-guest chemistry [6,7], and proton-coupled electron transfer processes [8]. Although 2,2′-bipyridines are one of the most commonly used ligands for metals, their protonated forms, the mono- or di-protonated 2,2′-bipyridinium salts [9], are also used as an oxidizing agent [10,11], fluorinating agent [12], and ligand precursor for a palladium catalyst [13]. Protonated pyridinium salts are typically synthesized from the reaction of the corresponding pyridines with Brønsted acids. However, most of these acids (e.g., hydrochloric acid, tetrafluoroboric acid, and trifluoromethanesulfonic acid (TfOH)) are corrosive, toxic, and difficult to handle. Therefore, it is desirable to develop an alternative method to avoid the direct use of such acids.

During the course of our study on 4,4′-Di-*tert*-butyl-2,2′-bipyridine-based early transition metal complexes [14–21], we developed interest in synthesizing a new scandium(III) complex using a scandium(III) salt and 4,4′-Di-*tert*-butyl-2,2′-bipyridine (4,4′-^{t}Bubpy; **1**). Among the scandium(III) salts, scandium(III) trifluoromethanesulfonate (Sc(OTf)$_3$) is an efficient and stable Lewis acid catalyst that maintains its catalytic activity even in the presence of water [22]. In addition, Sc(OTf)$_3$ has recently been used in combination with chiral nitrogen-donor ligands to achieve various enantioselective transformations [23]. Hence, we examined the complexation of 4,4′-^{t}Bubpy (**1**) with Sc(OTf)$_3$. Unexpectedly, however, we found that a mono-protonated bipyridinium trifluoromethanesulfonate **2** was obtained instead of a scandium bipyridine complex under the reaction conditions described later (Section 2). We herein report the synthesis of the new mono-protonated bipyridinium trifluoromethanesulfonate **2** without the direct use of TfOH.

2. Results and Discussion

Reaction of **1** with Sc(OTf)$_3$ in acetonitrile at ambient temperature afforded a pale pink solution. Subsequent addition of undried diethyl ether to this solution resulted in the formation of a white precipitate. Characterization of the compound revealed that the expected scandium bipyridine complex was not formed; instead, mono-protonated bipyridinium trifluoromethanesulfonate **2** was formed (Scheme 1).



Scheme 1. Synthesis of bipyridinium salt **2**.

The ^{1}H NMR spectrum of **2** in $CDCl_3$ shows three signals in the aromatic region at δ 8.88 (d, *J* = 5.6 Hz, 2H), 8.50 (d, *J* = 1.6 Hz, 2H), and 7.72 (dd, *J* = 5.6, 1.6 Hz, 2H), and these signals are shifted downfield with respect to those of **1** (Figure 1). This suggests the existence of a protonated nitrogen atom in **2** [13] (^{1}H, ^{13}C{^{1}H} and ^{19}F{^{1}H} NMR spectra of **2** are included in the Supplementary Materials). We also obtained long plate-like crystals by slow diffusion of diethyl ether into the acetonitrile solution of **2**. Although the obtained crystals were not of good quality, preliminary X-ray structure analysis of the crystals has confirmed the molecular structure of **2**.

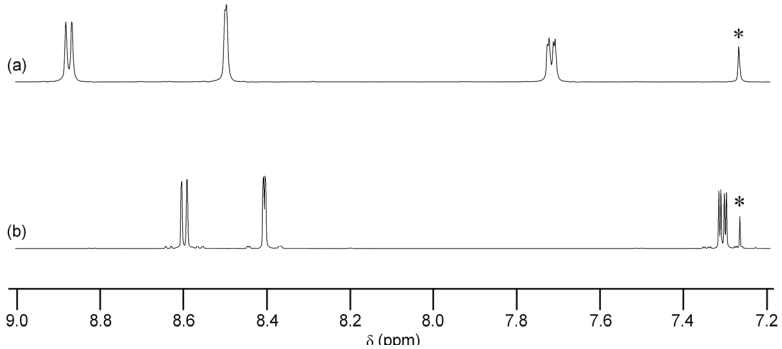


Figure 1. ^{1}H NMR spectra ($CDCl_3$) of (**a**) **2** and (**b**) **1** in the aromatic region (δ 9.0–7.2). The residual solvent signal of $CDCl_3$ is marked with an asterisk (∗).

Although $Sc(OTf)_3$ is often used as a stable Lewis acid even in water [22], this salt reversibly converts to TfOH through the hydrolysis of Sc^{3+} [24,25]. In the present reaction, we speculate that $Sc(OTf)_3$ reacts with the water in the reaction solvent to reversibly generate TfOH, followed by protonation of **1** to afford **2**. Bipyridinium salt **2** has low solubility in an acetonitrile–diethyl ether mixture and readily precipitates in the mixed solvent, shifting the reaction equilibrium to the product **2** side. Although it has already been known that the protonation of a pyridine derivative occurs in the presence of $Sc(OTf)_3$ and water in organic solvent [24], to our knowledge the preparation of protonated pyridinium trifluoromethanesulfonates based on this mechanism has not been explored. The protocol presented herein will provide safe and simple access not only to mono-protonated bipyridinium trifluoromethanesulfonates but also to a variety of protonated pyridinium trifluoromethanesulfonates without the direct use of TfOH.

3. Materials and Methods

3.1. General

All the reagents and solvents were purchased from chemical companies and used without further purification. ^{1}H NMR spectra were recorded on a JEOL JNM-ECS400 (400 MHz) FT NMR system or JEOL JMN-ECX400 (400 MHz) FT NMR system in $CDCl_3$ with Me_4Si as an internal standard. ^{13}C{^{1}H} NMR spectrum was recorded on a JEOL JNM-ECS400 (100 MHz) FT NMR system in $CDCl_3$. ^{19}F{^{1}H} NMR spectrum was recorded on a Bruker AVANCE NEO 400 spectrometer (376 MHz). The IR spectrum was recorded on a JASCO FT/IR-410 spectrometer.

*3.2. Synthesis of 4,4′-Di-tert-butyl-2,2′-bipyridinium Trifluoromethanesulfonate (**2**)*

Scandium(III) trifluoromethanesulfonate (247.5 mg, 0.5 mmol) and 4,4′-Di-*tert*-butyl-2,2′-bipyridine (**1**; 406.2 mg, 1.5 mmol) were stirred in acetonitrile (2.5 mL) at ambient temperature for 2 h. Diethyl ether was added to the resulting pale pink solution, and a white precipitate was obtained. The precipitate was collected and washed with diethyl ether to give **2** (270.8 mg, 43% yield based on **1**) as a white powder. Mp 216.5–217.0 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.88 (d, *J* = 5.6 Hz, 2H), 8.50 (d, *J* = 1.6 Hz, 2H), 7.72 (dd, *J* = 5.6, 1.6 Hz, 2H), 1.47 (s, 18H) [Note: The proton (H^+) signal of compound **2** could not be observed in the range of −2.5 to 20.5 ppm. This might be due to the rapid proton exchange of N–H.]; ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 168.0, 148.1, 146.2, 123.8, 120.6, 120.4 (q, *J* = 318.8 Hz), 36.2, 30.2; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −78.2; IR (KBr, cm^{-1}) 3104, 2974, 1631, 1597, 1485, 1442, 1284, 1266, 1227, 1206, 1153, 1035, 848; Anal. Calcd for $C_{19}H_{25}F_3N_2O_3S$: C, 54.53; H, 6.02; N, 6.69. Found: C, 54.61; H, 5.89; N, 6.57.

4. Conclusions

The new mono-protonated bipyridinium trifluoromethanesulfonate **2** has been synthesized from 4,4′-^{t}Bubpy using $Sc(OTf)_3$ without the direct use of TfOH. We consider that the present protocol will provide easy and safe access to a variety of protonated pyridinium trifluoromethanesulfonates.

Supplementary Materials: The following are available: Figure S1. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **2**. Figure S2. ^{13}C{^{1}H} NMR spectrum ($CDCl_3$, 100 MHz) of compound **2**. Figure S3. ^{19}F{^{1}H} NMR spectrum ($CDCl_3$, 376 MHz) of compound **2**.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Corey, E.J.; Suggs, J.W. Pyridinium chlorochromate. An efficient reagent for oxidation of primary and secondary alcohols to carbonyl compounds. *Tetrahedron Lett.* **1975**, *16*, 2647–2650. [CrossRef]
2. Nugent, B.M.; Yoder, R.A.; Johnston, J.N. Chiral Proton Catalysis: A Catalytic Enantioselective Direct Aza-Henry Reaction. *J. Am. Chem. Soc.* **2004**, *126*, 3418–3419. [CrossRef] [PubMed]
3. Takenaka, N.; Chen, J.; Captain, B.; Sarangthem, R.S.; Chandrakumar, A. Helical Chiral 2-Aminopyridinium Ions: A New Class of Hydrogen Bond Donor Catalysts. *J. Am. Chem. Soc.* **2010**, *132*, 4536–4537. [CrossRef] [PubMed]
4. Nishikawa, Y.; Nakano, S.; Tahira, Y.; Terazawa, K.; Yamazaki, K.; Kitamura, C.; Hara, O. Chiral Pyridinium Phosphoramide as a Dual Brønsted Acid Catalyst for Enantioselective Diels–Alder Reaction. *Org. Lett.* **2016**, *18*, 2004–2007. [CrossRef]
5. Ling, R.; Yoshida, M.; Mariano, P.S. Exploratory Investigations Probing a Preparatively Versatile, Pyridinium Salt Photoelectrocyclization−Solvolytic Aziridine Ring Opening Sequence. *J. Org. Chem.* **1996**, *61*, 4439–4449. [CrossRef] [PubMed]
6. Han, Y.; Meng, Z.; Chen, C.-F. Acid/base controllable complexation of a triptycene-derived macrotricyclic host and protonated 4,4′-bipyridinium/pyridinium salts. *Chem. Commun.* **2016**, *52*, 590–593. [CrossRef] [PubMed]

7. Li, J.; Shi, Q.; Han, Y.; Chen, C.-F. Complexation of 2,6-helic[6]arene and its derivatives with 1,1′- dimethyl-4,4′-bipyridinium salts and protonated 4,4′-bipyridinium salts: An acid−base controllable complexation. *Beilstein J. Org. Chem.* **2019**, *15*, 1795–1804. [CrossRef] [PubMed]
8. Pannwitz, A.; Wenger, O.S. Photoinduced Electron Transfer Coupled to Donor Deprotonation and Acceptor Protonation in a Molecular Triad Mimicking Photosystem II. *J. Am. Chem. Soc.* **2017**, *139*, 13308–13311. [CrossRef]
9. Beattie, I.R.; Webster, M. The Base Strengths of 2,2′-Bipyridyl and 1,10-Phenanthroline. *J. Phys. Chem.* **1962**, *66*, 115–116. [CrossRef]
10. Guziec, F.S.; Luzzio, F.A. The Oxidation of Alcohols Using 2,2′-Bipyridinium Chlorochromate. *Synthesis* **1980**, *9*, 691–694. [CrossRef]
11. Luzzio, F.A.; Bobb, R.A. 2,2′-Bipyrldinium Chlorochromate/*m*-Chloroperbenzoic Acid-Mediated Cleavage of Cyclic Acetals to Hydroxyesters. *Tetrahedron Lett.* **1997**, *38*, 1733–1736. [CrossRef]
12. Adachi, K.; Ohira, Y.; Tomizawa, G.; Ishihara, S.; Oishi, S. Electrophilic fluorination with *N*,*N*′-difluoro-2,2′-bipyridinium salt and elemental fluorine. *J. Fluorine Chem.* **2003**, *120*, 173–183. [CrossRef]
13. Milani, B.; Anzilutti, A.; Vicentini, L.; Sessanta o Santi, A.; Zangrando, E.; Geremia, S.; Mestroni, G. Bis-Chelated Palladium(II) Complexes with Nitrogen-Donor Chelating Ligands are Efficient Catalyst Precursors for the CO/Styrene Copolymerization Reaction. *Organometallics* **1997**, *16*, 5064–5075. [CrossRef]
14. Kodama, S.; Hashidate, S.; Nomoto, A.; Yano, S.; Ueshima, M.; Ogawa, A. Vanadium-catalyzed Atmospheric Oxidation of Benzyl Alcohols Using Water as Solvent. *Chem. Lett.* **2011**, *40*, 495–497. [CrossRef]
15. Kodama, S.; Nomoto, A.; Yano, S.; Ueshima, M.; Ogawa, A. Novel Heterotetranuclear V_2Mo_2 or V_2W_2 Complexes with 4,4′-Di-*tert*-butyl-2,2′-bipyridine: Syntheses, Crystal structures, and Catalytic Activities. *Inorg. Chem.* **2011**, *50*, 9942–9947. [CrossRef] [PubMed]
16. Marui, K.; Higashiura, Y.; Kodama, S.; Hashidate, S.; Nomoto, A.; Yano, S.; Ueshima, M.; Ogawa, A. Vanadium-catalyzed green oxidation of benzylic alcohols in water under air atmosphere. *Tetrahedron* **2014**, *70*, 2431–2438. [CrossRef]
17. Kodama, S.; Taya, N.; Ishii, Y. A Novel Octanuclear Vanadium(V) Oxide Cluster Complex Having an Unprecedented Neutral V_8O_{20} Core Functionalized with 4,4′-Di-*tert*-butyl-2,2′- bipyridine. *Inorg. Chem.* **2014**, *53*, 2754–2756. [CrossRef] [PubMed]
18. Kodama, S.; Taya, N.; Inoue, Y.; Ishii, Y. Synthesis and Interconversion of V_4, V_7, and V_8 Oxide Clusters: Unexpected Formation of Neutral Heptanuclear Oxido(alkoxido)vanadium(V) Clusters $[V_7O_{17}(OR)(4,4'\text{-}^t\text{Bubpy})_3]$ (R = Et, $MeOC_2H_4$). *Inorg. Chem.* **2016**, *55*, 6712–6718. [CrossRef]
19. Kobayashi, D.; Kodama, S.; Ishii, Y. An Oxidovanadium(IV) Complex Having a Perrhenato Ligand: An Efficient Catalyst for Aerobic Oxidation Reactions of Benzylic and Propargylic Alcohols. *Tetrahedron Lett.* **2017**, *58*, 3306–3310. [CrossRef]
20. Inoue, Y.; Kodama, S.; Taya, N.; Sato, H.; Oh-ishi, K.; Ishii, Y. Reductive Formation of a Vanadium(IV/V) Oxide Cluster Complex $[V_8O_{19}(4,4'\text{-}^t\text{Bubpy})_3]$ Having a C_3-Symmetric Propeller-Shaped Nonionic V_8O_{19} Core. *Inorg. Chem.* **2018**, *57*, 7491–7494. [CrossRef]
21. Kodama, S.; Kondo, S.; Nomoto, A.; Ogawa, A. Tris(4,4′-di-*tert*-butyl-2,2′-bipyridine)(*trans*-4-*tert*-butylcyclohexanolato)deca-μ-oxido-heptaoxidoheptavanadium acetonitrile monosolvate including another unknown solvent molecule. *IUCrData* **2020**, *5*, x200449. [CrossRef]
22. Kobayashi, S. Scandium Triflate in Organic Synthesis. *Eur. J. Org. Chem.* **1999**, *1999*, 15–27. [CrossRef]
23. Pellissier, H. Recent developments in enantioselective scandium-catalyzed transformations. *Coord. Chem. Rev.* **2016**, *313*, 1–37. [CrossRef]
24. Wabnitz, T.C.; Yu, J.-Q.; Spencer, J.B. Evidence That Protons Can Be the Active Catalysts in Lewis Acid Mediated HeteroMichael Addition Reactions. *Chem. Eur. J.* **2004**, *10*, 484–493. [CrossRef] [PubMed]
25. Šolić, I.; Seankongsuk, P.; Loh, J.K.; Vilaivan, T.; Bates, R.W. Scandium as a pre-catalyst for the deoxygenative allylation of benzylic alcohols. *Org. Biomol. Chem.* **2018**, *16*, 119–123. [CrossRef] [PubMed]