ChemComm

RSC Publishing

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Chem. Commun.*, 2013, **49**, 1109

Received 27th October 2012,
Accepted 17th December 2012

DOI: 10.1039/c2cc37801a

www.rsc.org/chemcomm

Activation of dichloromethane by a V(III) thiolate complex: an example of S-based nucleophilic reactivity in an early transition metal thiolate†

Tzu-Tso Chen,‡[a] Yu-Sen Chen,‡[a] Ya-Ho Chang,[a] Jung-Ching Wang,[a] Yi-Fang Tsai,[a] Gene-Hsiang Lee,[b] Tin-Shen Kuo[c] and Hua-Fen Hsu*[a]

A V^{III} thiolate complex activated C–Cl bond in dichloromethane *via* S-based nucleophilic attack. The reaction products, a V^{III}-Cl species (major one) and a V^{IV} binding to a CH_2 containing ligand (minor one) were obtained. The work demonstrates sulfur donors in the early-transition metal thiolates having strong nucleophilic characteristics.

The non-innocent nature of cysteine bioligand has yielded a wide range of sulfur-based reactivity in biological systems, such as the post-translational modifications of nitrile hydratase,[1] cysteine dioxygenase,[2] and Zn^{II}-dependent thiolate methylation proteins. The last one has involved S-alkylation of cysteine identified in DNA repair protein Ada,[3] methionine synthase,[4] and farnesyl transferase.[5] In synthetic examples, the alkylation of metal bound sulfur donor has been mostly found in various late-transition metal thiolates, for instance, in the cases of Cu^{I}, Ni^{II}, Zn^{II}, Fe^{II}, Ru^{II} and Pt^{II} complexes.[6] These comply with a hypothesis that the nucleophilicity of the metal bound sulfur donor is a result of the four-electron destabilizing interaction of lone pairs on thiolate sulfur and fulfilled metal d-orbitals.[7a] Recently, a more detailed mechanism has been developed through studies involving zinc compounds or enzymes.[7b–d] These state that the active nucleopile might involve a dissociated/unbound thiolate or bound thiolate. Alternatively, the pathway might be based on a σ-bond metathesis reaction with a four-center transition state. By contrast, the alkylation of the bound sulfur in the early-transition metal thiolates has not been widely observed and investigated. The only reported example is a dimeric molybdenum complex that undergoes nucleophilic attack on dibromomethane to form a methylene-brideged thioether core.[8]

The increasing interest in vanadium sulfur complex stems from its biological relevance, specifically, the interaction between vanadium ion and cysteine or glutathione as well as the finding of vanadium nitrogenase.[9] For examples, cysteine and glutathione might act as reductants for the intracellar reduction of vanadium ion in vanadocyte of ascidians.[10] Amavadin, a natural V^{IV} complex likely plays a role in the fungus defensive system through the specific oxidation of some thiols to disulfide.[11] In the cases of vanadium ion interacting with organic thiolate ligands, the sulfur donors mainly behave as innocent ligands and act as structural support. However, in several examples, the thiolate ligands are not innocent and display several types of reactivity.[12] These include the formation of a disulfide bond coupled with the reduction of vanadium ion,[12a,b] the oxygenation of the bound sulfur in a V^{V}-thiolate resulting in a corresponding sulfenate compound[12c] and the generation of a metal–thiyl radical that further cleaves the C–O bond of methanol, consequently leading to the methylation of the bound thiolate.[12b,d] It was proposed that a vanadyl(IV) *cis*-dithiolate complex reacting with 1,3-dibromopropane might generate an S-alkylated product, however no direct evidence was provided for this chemistry.[13] At this work, we report a V^{III}-thiolate complex that shows S-based nucleophilic reactivity with dichloromethane (Scheme 1). Such reactivity is rare for early-transition metal thiolates and unprecedented for the existing vanadium thiolate complexes.

A six-coordinate V^{III} complex, $[V^{III}(PS2S^{H\prime\prime})_2][PPh_4]$ (**1**), was obtained from the reaction of $VCl_3(thf)_3$ and $[PS2S^{H\prime\prime}]^{2-}$ in a 1 : 2 ratio ($[PS2S^{H\prime\prime}]^{2-}$ = $P(C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_2(C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}SH)$). The addition of the counterion, PPh_4^+, to the reaction mixture, followed by layering with ether, gave the crystalline solid of **1**·0.103CH_3OH·0.455THF (60% yield). The X-ray crystallographic data shows **1** as a distorted octahedral vanadium center by way of its binding to two $[PS2S^{H\prime\prime}]^{2-}$ ligands where thiol groups remain unbound (Fig. 1).§ The electron density of the hydrogen atoms in the unbound thiols was not found in diffraction map, however, the distance of 3.642 Å between S2 and S6 atoms indicates the presence of intramolecular hydrogen bonding interaction. The containing thiol groups in **1** were also supported by an IR spectrum that gave an S–H stretching band at 2312 cm^{-1} (Fig. S1 in the ESI†). In addition, FAB-mass data show a set of

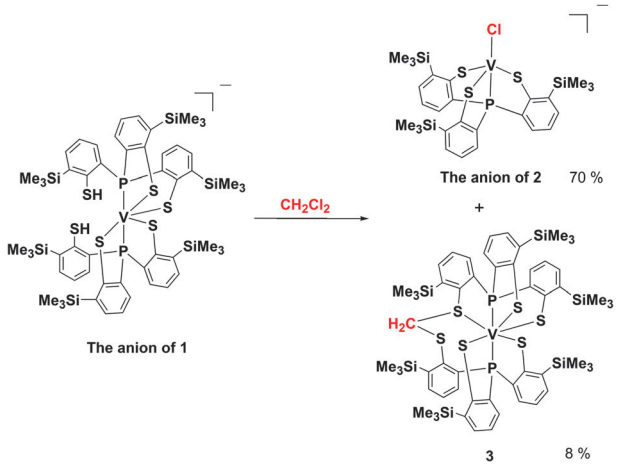
[a] *Department of Chemistry, National Cheng Kung University, Tainan 701, Taiwan. E-mail: konopka@mail.ncku.edu.tw; Fax: +886-62740552; Tel: +886-62757575-65336*

[b] *Department of Chemistry, National Taiwan University, Taipei 116, Taiwan*

[c] *Department of Chemistry, National Taiwan Normal University, Taipei 116, Taiwan*

† Electronic Supplementary Information (ESI) available: Experimental details, IR spectrum of **1**, UV-vis-NIR spectrum of **3**, X-ray structural parameters and selected bond distances and angles of **1** and **3**. CCDC 895276 and 895067. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc37801a

‡ T.-T. C and Y.-S. C. contributed equally.



Scheme 1

peaks at 1195 *m*/*z*, consistent with the calculated mass of the isotope pattern of $[V^{III}(PS2S^{H''})_2]^-$ (the anion of **1**).

Dissolving complex **1** in CH_2Cl_2 yielded a reddish-brown solution, but the color gradually turned to yellow in 24 h. Continuously layered with hexane, the crystals of $[V^{III}(PS3'')Cl]$-$[PPh_4]$ (**2**) ($[PS3'']^{3-}$ = $P(C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3$) were precipitated in 3–5 days (70% yield based on vanadium).

When methanol was used instead of hexane to layer on dichloromethane solution of **1**, the crystalline form of $[V^{IV}((PS3'')_2{}^{CH2})]$ (**3**), was produced (8% yield based on vanadium) (Scheme 1). In control experiments, the reaction carried in the absence of light gave the same products, excluding the involvement of the photolysis. Complex **2** has been reported previously by our laboratory.[14] It consists of a five-coordinate V^{III} center ligated by a chloride and a PS3″ ligand, forming a trigonal bipyramidal geometry. The X-ray crystallographic structure of **3** was obtained and it adopts a seven-coordinate V^{IV} center by binding to a $((PS3'')_2{}^{CH2})$ ligand, where a methylene group is bridged between two thiolates of two PS3″ ligands (Fig. 2). The geometry found in **3** is a distorted pentagonal bipyramid with S2 and S6 thiolato groups in axial positions (S2–V1–S6 = 168.07 deg). The equatorial plane is constructed by two phosphine donors (P1 and P2), two thiolates (S1 and S3) and one thioether (S5).

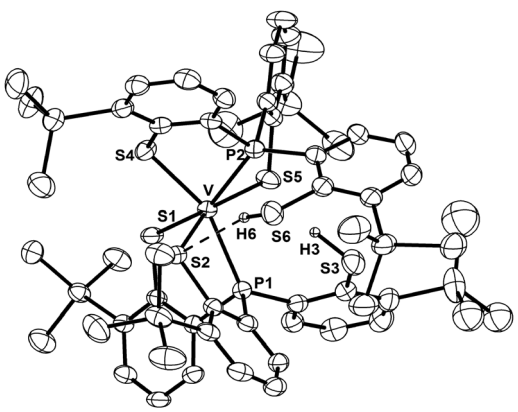


Fig. 1 Thermal ellipsoid plot (35% probability) of **1**·0.103CH_3OH·0.455THF. The H atoms except H3 and H6, cation (PPh_4^+), and solvated molecules are omitted for clarity.

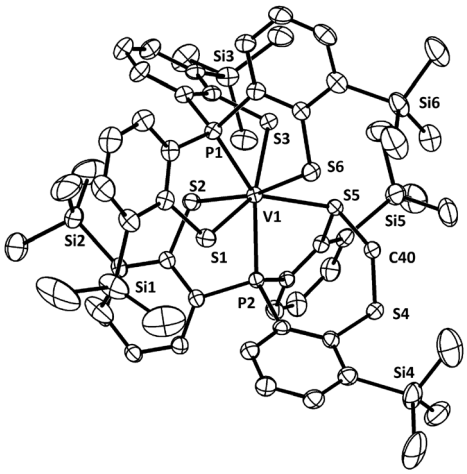


Fig. 2 Thermal ellipsoid plot (35% probability) of $[V^{IV}((PS3'')_2{}^{CH2}]$ (**3**). H atoms are omitted for clarity.

The isolation of **2** and **3** from the reaction of **1** with dichloromethane is consistent with activation and cleavage of the C–Cl bond and insertion of the methylene moiety of dichloromethane between two S-donors of two different PS3″ ligands, forming a methylene-bridged thioether core contained in $[V^{IV}((PS3'')_2{}^{CH2})]$ (**3**). Confidence in this interpretation of the nature of the reaction was enhanced by ESI-MS spectrometric investigations. Thus, complex **3** gives rise to a set of molecular ion peaks at 1208 *m*/*z* $(M + H)^+$, consistent with the theoretical isotope pattern. When CD_2Cl_2 was used instead of CH_2Cl_2 in the reaction, the molecular ion peaks were shifted by 2 *m*/*z* with the same isotope pattern (Fig. 3), unequivocally meaning that the bridged methylene moiety is from the cleavage of dichloromethane.

The conversion of **1** in dichloromethane solution to **2** was also demonstrated by UV-vis-NIR and ^1H NMR spectroscopic studies. As shown in Fig. 4, the electronic spectrum of **1** in CH_2Cl_2 slowly changed to the one with characteristic bands similar to those in **2** during a 24 hour observation. A nearly complete conversion

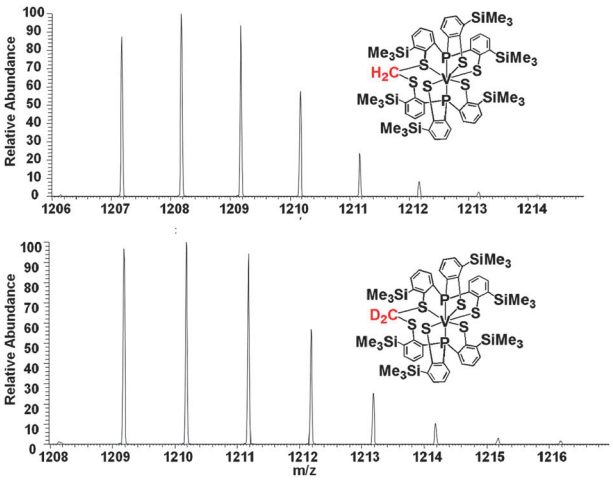


Fig. 3 ESI-MS spectrum of complex **3** (top) and complex **3** isolated from the reaction of **1** and CD_2Cl_2 (bottom). The molecular ion peaks display isotopic distribution at 1207 *m*/*z* (top) and 1209 *m*/*z* (bottom), consistent with the formulation of $C_{55}H_{74}P_2S_6Si_6V_1$ and $C_{55}D_2H_{72}P_2S_6Si_6V_1$, respectively.

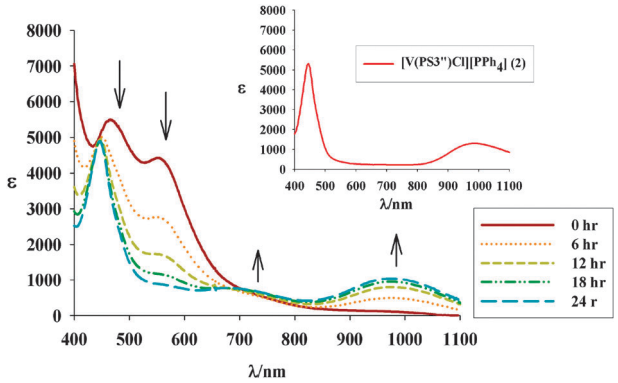


Fig. 4 Variation in UV-vis-NIR spectrum of **1** in CH_2Cl_2 (3.18×10^{-4} M). The spectrum was taken every 6 hour during a 24 hour time period. Inset: UV-vis-NIR spectrum of **2** in CH_2Cl_2.

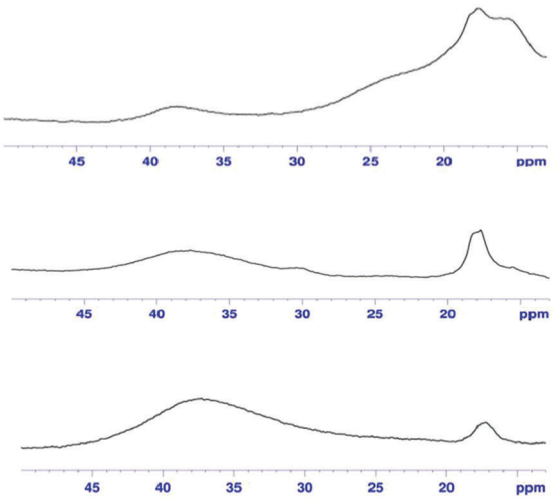


Fig. 5 ^{1}H-NMR spectra of Complex **1** disolved in CD_2Cl_2 initially (top) and after 24 h (middle). Complex **2** in CD_2Cl_2 (bottom).

of **1** to **2** is marked by an isobestic point at 680 nm. The broad band appearing around 600 nm to 800 nm in the final spectrum that is absent in the spectrum of **2** is attributed to the formation of the minor product, complex **3** (Fig. S2 in the ESI†). This result was also supported by ^{1}H-NMR spectra, as displayed in Fig. 5. The spectrum of **1** dissolved in CD_2Cl_2 exhibits a broad band at 15–20 ppm initially, but gradually became smaller and sharper. The broad band at 30–45 ppm was also more pronounced. The final spectrum after 24 hours displayed features similar to that of **2** dissolved in CD_2Cl_2.

In conclusion, this work demonstrated that a V^{III} thiolate complex, **1**, can activate a C–Cl bond in dichloromethane *via* the sulfur-based nucleophilicity. The reaction led to the formation of a major product containing a chloride bound donor and a minor one with a ligand containing a methylene-bridged thioether core. As such chemistry is often reported for the late-transition metal thiolate complexes, our results give an implication that sulfur donors in the early-transition metal thiolates also have strong nucleophilic characteristics reacting with a weak electrophile such as dichloromethane. Whether the active nucleophile of this reaction involves a bound thiolate or a dissociated thiolato ligand is still obscure with the current data. The kinetic study and theoretic calculation of this chemistry are undergoing to provide the further mechanistic information.

This work was supported by National Science Council in Taiwan (NSC 99-2113-M006-004-MY3).

Notes and references

§ Crystal data for **1**·0.103CH_3OH·0.455THF: CCDC-895276, $C_{79.93}H_{98.07}O_{0.56}P_3S_6Si_6V$, M = 1572.52, triclinic, space group $P\bar{1}$ (no. 2), a = 13.2824(2) Å, b = 16.9608(3) Å, c = 20.7372(3) Å, α = 80.6212(11)°, β = 86.5684(12)°, γ = 70.7773(7)°, V = 4352.15(12) Å^3, Z = 2, $d_{(calcd)}$ = 1.200 Mg m^{-3}, T = 150 K, 67094 reflection collected, 19900 independent, R_{int} = 0.0565, R_1 = 0.0560, wR_2 = 0.1456 for all data. Crystal data for **3**: CCDC-895067, $C_{55}H_{74}P_2S_6Si_6V$, M = 1208.92, monoclinic, space group $P2_1/c$ (no. 14), a = 26.551(8) Å, b = 11.965(4) Å, c = 21.288(6) Å, α = 90°, β = 104.2(5)°, γ = 90°, V = 6556.03(300) Å^3, Z = 4, $d_{(calcd)}$ = 1.225 Mg m^{-3}, T = 296(2) K, 16135 reflection collected, 7071 independent, R_{int} = 0.1902, R_1 = 0.0634, wR_2 = 0.1151 for all data.

1 J. A. Kovacs, *Chem. Rev.*, 2004, **104**, 825.
2 J. D. Gardner, B. S. Pierce, B. G. Fox and T. C. Brunold, *Biochemistry*, 2010, **49**, 6033.
3 T. Lindahl, *Nature*, 1993, **362**, 709.
4 K. Peariso, Z. S. Zhou, A. E. Smith, R. G. Matthews and J. E. Penner-Hahn, *Biochemistry*, 2001, **40**, 987.
5 D. A. Tobin, J. S. Pickett, H. L. Hartman, C. A. Fierke and J. E. Penner-Hahn, *J. Am. Chem. Soc.*, 2003, **125**, 9962.
6 (*a*) Q. Wang, A. C. Marr, A. J. Blake, C. Wilson and M. Schroder, *Chem. Commun.*, 2003, 2776; (*b*) C. A. Grapperhaus, S. Poturovic and M. S. Mashuta, *Inorg. Chem.*, 2002, **41**, 4309; (*c*) C.-W. Chang, Y.-C. Lin, G.-H. Lee and Y. Wang, *Organometallics*, 2003, **22**, 3891; (*d*) V. W. W. Yam, P. K. Y. Yeung and K. K. Cheung, *J. Chem. Soc., Chem. Commun.*, 1995, 267; (*e*) Z. Li, W. Zheng, H. Liu, K. F. Mok and T. S. A. Hor, *Inorg. Chem.*, 2003, **42**, 8481; (*f*) J. R. Bleeke, M. Shokeen, E. S. Wise and N. P. Rath, *Organometallics*, 2006, **25**, 2486; (*g*) D. Sellmann, M. Waeber, H. Binder and R. Boese, *Zeitschrift Fur Naturforschung Section B-a Journal of Chemical Sciences*, 1986, **41**, 1541; (*h*) D. C. Fox, A. T. Fiedler, H. L. Halfen, T. C. Brunold and J. A. Halfen, *J. Am. Chem. Soc.*, 2004, **126**, 7627; (*i*) M. Gennari, M. Retegan, S. DeBeer, J. Pécaut, F. Neese, M.-N. Collomb and C. Duboc, *Inorg. Chem.*, 2011, **50**, 10047; (*j*) M. Gennari, J. Pécaut, S. DeBeer, F. Neese, M.-N. Collomb and C. Duboc, *Angew. Chem., Int. Ed.*, 2011, **50**, 5662.
7 (*a*) M. T. Ashby, J. H. Enemark and D. L. Lichtenberger, *Inorg. Chem.*, 1988, **27**, 191; (*b*) J. Penner-Hahn, *Curr. Opin. Chem. Biol.*, 2007, **11**, 166; (*c*) G. Parkin, *Chem. Rev.*, 2004, **104**, 699; (*d*) D. Picot, G. Ohanessian and G. Frison, *Inorg. Chem.*, 2008, **47**, 8167.
8 M. McKenna, L. L. Wright, D. J. Miller, L. Tanner, R. C. Haltiwanger and M. R. DuBois, *J. Am. Chem. Soc.*, 1983, **105**, 5329.
9 (*a*) D. C. Crans, J. J. Smee, E. Gaidamauskas and L. Yang, *Chem. Rev.*, 2004, **104**, 849; (*b*) D. Rehder, *Bioinorganic Vanadium Chemistry; John Wiley & Sons*, 2008.
10 T. Ueki and H. Michibata, *Coord. Chem. Rev.*, 2011, **255**, 2249–2257.
11 C. D. Garner, E. M. Armstrong, R. E. Berry, R. L. Beddoes, D. Collison, J. J. A. Cooney, S. N. Ertok and M. Helliwell, *J. Inorg. Biochem.*, 2000, **80**, 17.
12 (*a*) D. Wang, A. Behrens, M. Farahbakhsh, J. Gätjens and D. Rehder, *Chem.–Eur. J.*, 2003, **9**, 1805; (*b*) H.-F. Hsu, C.-L. Su, N. O. Gopal, C.-C. Wu, W.-C. Chu, Y.-F. Tsai, Y.-H. Chang, Y.-H. Liu, T.-S. Kuo and S.-C. Ke, *Eur. J. Inorg. Chem.*, 2006, 1161; (*c*) C. R. Cornman, T. C. Stauffer and P. D. Boyle, *J. Am. Chem. Soc.*, 1997, **119**, 5986; (*d*) Y.-H. Chang, C.-L. Su, R.-R. Wu, J.-H. Liao, Y.-H. Liu and H.-F. Hsu, *J. Am. Chem. Soc.*, 2011, **133**, 5708.
13 R. M. Jenkins, T. A. Pinder, M. L. Hatley, J. H. Reibenspies and M. Y. Darensbourg, *Inorg. Chem.*, 2011, **50**, 1849.
14 W.-C. Chu, C.-C. Wu and H.-F. Hsu, *Inorg. Chem.*, 2006, **45**, 3164.