Supporting Information for

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

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Experimental Section

General considerations: All procedures were carried out under dinitrogen with standard Schlenk techniques or glove box. Air-sensitive compounds or reagents were weighed out inside a glove box with control of static electricity. $[P(C_6H_3\text{-}3\text{-}Me_3Si\text{-}2\text{-}SH)_3]$,[1] and $VCl_3(THF)_3$[2] were synthesized according to the literature procedures. THF and ether were dried by distillation from Na/benzophenone. CH_2Cl_2 was dried by distillation from CaH_2 and P_2O_5. CH_3OH was dried by distillation from CaH_2. CH_3CN was dried by distillation from CaH_2 and P_2O_5, then passed through an activated alumina column. Otherwise all starting materials were obtained commercially and used without further purification.

Physical Method: Elemental analyses were measured with Elemetar vario EL III. The electrospray ionization (ESI) mass data were taken in CH_3CN with the LTQ Orbitrap XL, Thermo-Fisher spectrometer. The ^{1}H-NMR spectra were taken on a BRUKER AMX500 spectrometer. The samples were prepared in a sealed NMR tube under nitrogen atmosphere. Electronic spectra were recorded in the range of 190 nm to 1100 nm with Hewlett Packard 8453 spectrophotometer at room temperature. X-ray Crystallographic Data of complex 1 was collected at 150 K by Nonious Kappa CCD Single-crystal XRD equipped with Oxford Cryostream 700. Diffraction measurements of complex 3 were measured at 296 K by using a Nonius Kappa CCD diffractometer equipped with graphite-monochromated Mo-kα radiation (λ = 0.7173 Å). Least-squares refinement of the positional and anisotropic thermal parameters for the contribution of all non-hydrogen atoms and fixed hydrogen atoms was based on F2. A SADABS absorption correction was made.[1] The SHELXTL structural refinement program was employed.[2] All the non-hydrogen atoms were refined with anisotropic displacement factors. All the hydrogen atoms are calculated by using the riding model.

Synthesis for $[V^{III}(PS_2S^{H}")_2][PPh_4]$ (1) • 0.103CH_3OH • 0.455THF

Utilizing $PS_3"H_3$ (0.308 g, 0.537 mmol) and Lithium (0.0075 g, 1.082mmol) dissolved in CH_3OH generated a pale yellow solution. Blending with $VCl_3(thf)_3$ (0.100 g, 0.268 mmol) in THF, the reddish-brown solution appeared. The addition of PPh_4Br (0.112 g, 0.268 mmol) followed by layering with ether gave a crystalline solid of **1** after 3 days. Yield: 0.246 g, 60% (based on $VCl_3(thf)_3$). Anal. Calcd for $C_{78}H_{94}P_3S_6Si_6V$: C, 60.98; H, 6.17; S, 12.52. Found: C 60.81, H 6.20, S 12.05. UV-Vis-NIR (CH_3CN) λ_{max}, nm (ε, $M^{-1}cm^{-1}$): 465 (5500), 553 (4400). FAB-MS(-),

m/z for $C_{54}H_{74}P_2S_6Si_6V$, $[M]^-$ 1195.17 calcd, 1195.16 found. FTIR (KBr pellet cm^{-1}): 3033, 2946, 2891, 2312, 1586, 1552, 1483, 1436, 1355, 1240, 1997, 1144, 1105, 1041, 997, 928, 852, 834, 782, 754, 722, 687, 624, 543, 527, 485, 459.

Synthesis for $[V^{IV}((PS_3")_2{}^{CH2})]$ (3)

Method A: Dissolution of **1** (0.05g, 0.031mmol) in CH_2Cl_2 followed by layering with CH_3OH gave the precipitation of **3**. The blue powder of **3** was isolated from solution, 0.003 g, 8% yield (based on **1**) after 5 days. Method B: Utilizing $PS_3"H_3$ (0.308 g, 0.537 mmol) and Lithium (0.012 g, 1.732 mmol) dissolved in MeOH generated a pale yellow solution. Blending with $VCl_3(thf)_3$ (0.100 g, 0.268 mmol) in THF, the reddish-brown solution appeared. After exposure to the air, the solvent was removed. The solution color changed from reddish brown to gray. Continuously dried it and redissolved in dichloromethane, and followed by layering with MeOH gave blue columned crystals of **3** after 7 days later. Yield: 0.129 g, 40% (based on $VCl_3(thf)_3$). Anal. Calcd for $C_{55}H_{74}P_2S_6Si_6V$: C 56.64, H 6.17, S 15.91; found: C 54.59, H 6.19, S 15.87. Uv-Vis-NIR (CH_2Cl_2) λ_{max}, nm (ε, $M^{-1}cm^{-1}$): 492 (5800), 598 (5600), 642 (5700). ESI-MS(+), m/z for $C_{55}H_{75}P_2S_6Si_6V$, $[M+H]^+$ 1208.17 calcd, 1208.18 found.

Crystallographic data for $[V^{III}(PS2"S^H)_2][PPh_4] \cdot 0.103CH_3OH \cdot 0.455THF$ (1)

$C_{79.93}H_{98.07}O_{0.56}P_3S_6Si_6V$, M = 1572.52, triclinic, space group P-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, Rint = 0.0565, R_1 = 0.0560, wR_2 = 0.1456 for all data. CCDC-895276 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for $[V^{IV}((PS_3")_2{}^{CH2})]$ (3)

$C_{55}H_{74}P_2S_6Si_6V$, M = 1208.92, monoclinic, space group P21/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(3) $Å^3$, Z = 4, d(calcd) = 1.225 Mg/m^3, T = 296(2) K, 16135 reflection collected, 7071 independent, Rint = 0.1902, R_1 = 0.0634, wR_2 = 0.1151 for all data. CCDC-895067 contains the supplementary crystallographic data for this paper.

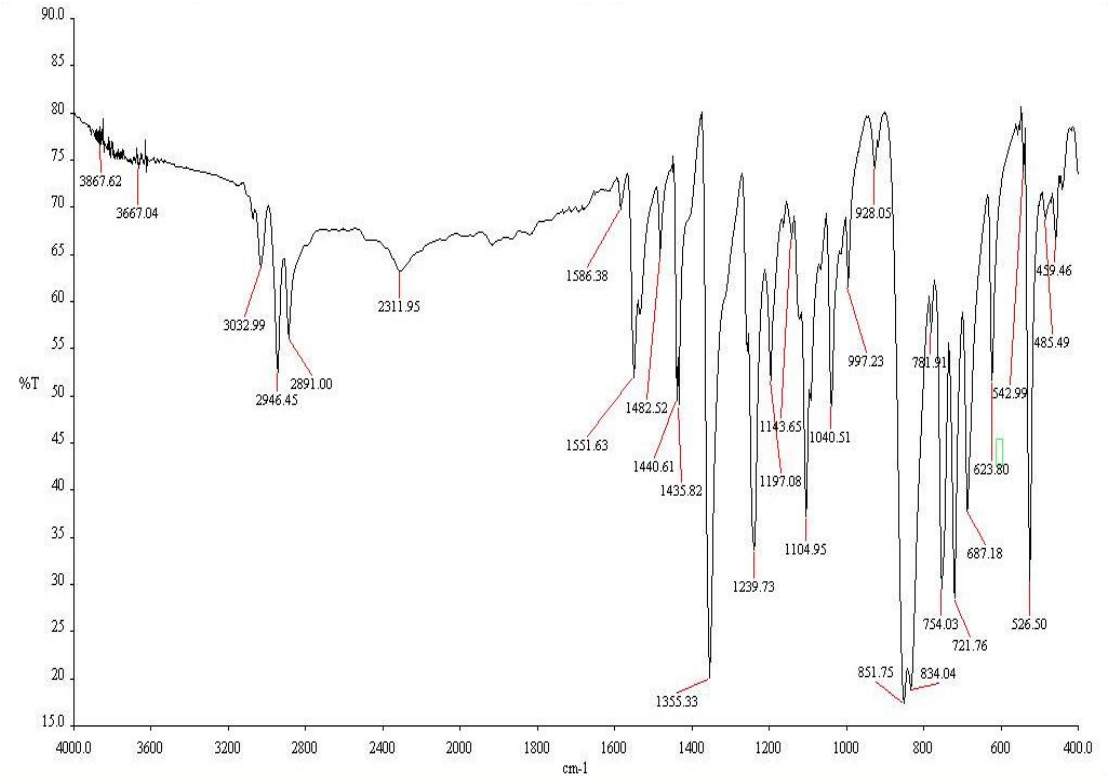

Figure S1. IR spectrum of $[V^{III}(PS2''S^{H})_2][PPh_4]$ (**1**)

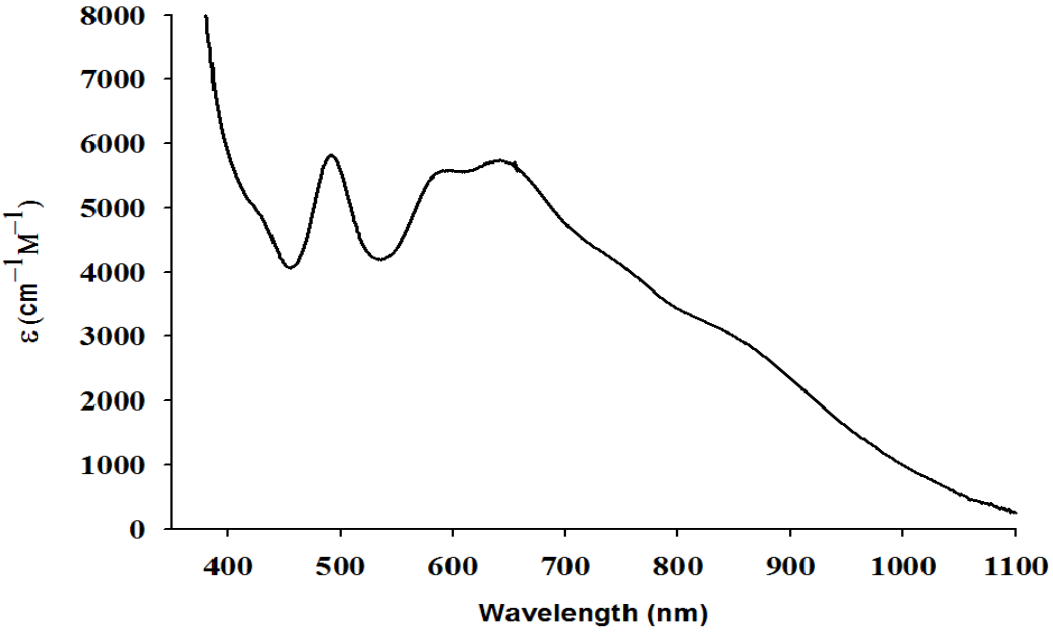

Figure S2. UV-vis-NIR spectrum of $[V^{IV}(PS3'')_2{}^{CH2}]$ **(3)**.

Table 1. X-ray Crystallographic Data for $[V^{III}(PS2''S^{H})_2][PPh_4]$ • **0.103**CH_3OH • **0.455**THF (**1**) and $[V^{IV}(PS3'')_2{}^{CH2}]$ **(3).**

	1 • **0.103**CH_3OH • **0.455**THF	**3**
Empirical formula	$C_{79.93}H_{98.07}O_{0.56}P_3S_6Si_6V$	$C_{55}H_{74}P_2S_6Si_6V$
Crystal size (mm)	0.50 × 0.20 × 0.16	1.971 × 0.281 × 0.142
Crystal Habit, colour	rod, red-brown	Column, blue
Crystal system	triclinic	monoclinic
Space group	P-1	$P2_1/c$
Volume (Å^3)	4352.15(12)	6556(3)
a (Å)	13.2824(2)	26.551(8)
b (Å)	16.9608(3)	11.965(4)
c (Å)	20.7372(3)	21.288(6)
α (°)	80.6212(11)	90
β (°)	86.5684(12)	104.204(5)
γ (°)	70.7773(7)	90
Z	2	4
Formula weight (g/mol)	1572.52	1208.92
Density (calculated) (Mg/m^3)	1.200	1.225
Absorption coefficient (mm^{-1})	0.436	0.534
F_{000}	1660	2548
Total no. reflections	67094	48085
Unique reflections	19900	16135
Final R indices (I > 2σ(I)]	R1 = 0.0560, wR2 = 0.1456	R1 = 0.0634, wR2 = 0.1151
Largest diff. peak and hole (e.Å^{-3})	1.200 and -0.665	0.626 and -0.564
GOF	1.070	0.929

$R_1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$; $w = 1/\sigma^2(|Fo|)$

Table 2. Selected bond distances (Å) and angles (deg) for $[V^{III}(PS2"S^{H})_2][PPh_4] \cdot 0.103CH_3OH \cdot 0.455THF$ (**1**).

Selected bond distances (Å)		**Selected bond angles (deg)**	
V1—S1	2.4061(9)	S1—V1—S2	102.00(3)
V1—S2	2.4210(9)	S1—V1—S4	87.90(3)
V1—S4	2.3943(9)	S1—V1—S5	93.71(3)
V1—S5	2.3643(9)	S2—V1—S4	86.12(3)
V1—P1	2.4553(9)	S2—V1—S5	155.78(4)
V1—P2	2.5303(9)	S4—V1—S5	113.04(3)
S2—S6	3.642(2)	P1—V1—S1	81.90(3)
		P1—V1—S2	75.87(3)
		P1—V1—S4	156.87(3)
		P1—V1—S5	88.41(3)
		P2—V1—S1	155.92(3)
		P2—V1—S2	94.52(3)
		P2—V1—S4	75.74(3)
		P2—V1—S5	77.11(3)
		P1—V1—P2	119.48(3)

Table 3. Selected bond distances (Å) and angles (deg) for $[V^{IV}(PS3'')_2^{CH2}]$ **(3).**

Selected bond distances (Å)		Selected bond angles (deg)	
V1—S1	2.390(1)	S1—V1—S2	89.05(5),
V1—S2	2.3844(1)	S1—V1—S3	148.19(5),
V1—S3	2.4204(1)	S1—V1—S5	136.92(5)
V1—S5	2.5598(1)	S1—V1—S6	91.33(5)
V1—S6	2.4493(1)	S2—V1—S3	81.13(4)
V1—P1	2.3841(1)	S2—V1—S5	108.62(5)
V1—P2	2.4827(1)	S2—V1—S6	168.07(5)
S4—C40	1.771(4)	S3—V1—S5	74.68(4)
S5—C40	1.871(4)	S3—V1—S6	92.39(5)
		S5—V1—S6	78.96(5)
		S4—C40—S5	118.4 (2)
		P1—V1—S1	78.85(5)
		P1—V1—S2	90.64(5)
		P1—V1—S3	71.14(4)
		P1—V1—S5	137.33(5)
		P1—V1—S6	77.74(5)
		P1—V1—P2	149.49(5)
		P2—V1—S1	74.54(4)
		P2—V1—S3	130.18(5)
		P2—V1—S5	73.18(4)
		P2—V1—S6	117.14(5)

Reference

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