Supporting Information for

Synthesis of (Adamantylmido)vanadium(V)-Alkyl, Alkylidene Complex Trapped with PMe_3: Reactions of the Alkylidene Complexes with Phenols

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Contents

1. NMR spectra for V(CHSiMe$_3$)(NAd)(CH$_2$SiMe$_3$)(PMe$_3$)$_2$ (1, Ad = 1-adamantyl), V(CHSiMe$_3$)(NAd)(O-2,6-Me$_2$C$_6$H$_3$)(PMe$_3$)$_2$ (2a) and some reaction chemistry (with phenols etc.).

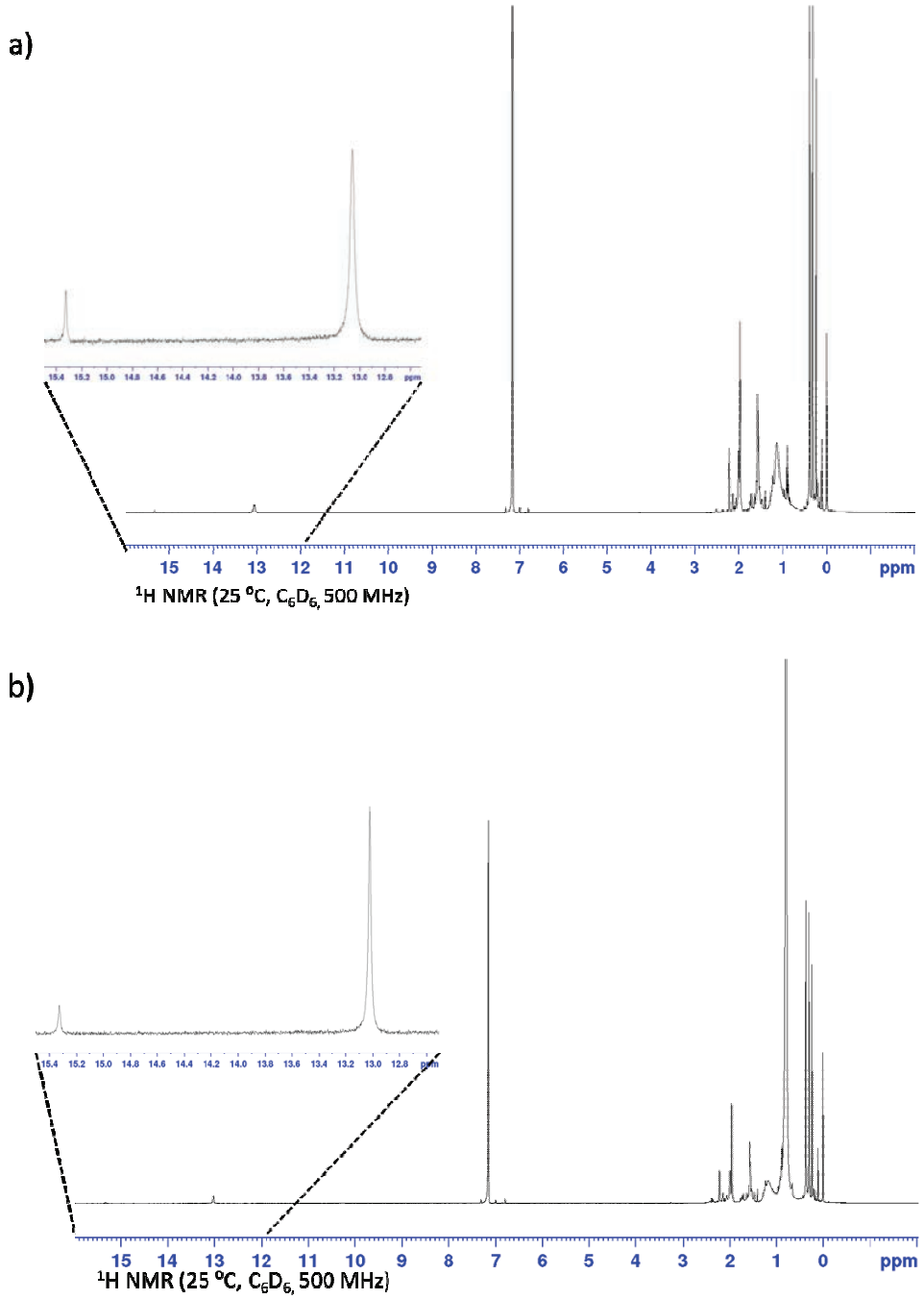

Figure S1-1. ^{1}H NMR spectra (25 ^{0}C, C_6D_6) of a) V(CHSiMe$_3$)(NAd)(CH$_2$SiMe$_3$)(PMe$_3$)$_2$ (**1**), b) 1 in the presence of PMe$_3$ (20 equiv).

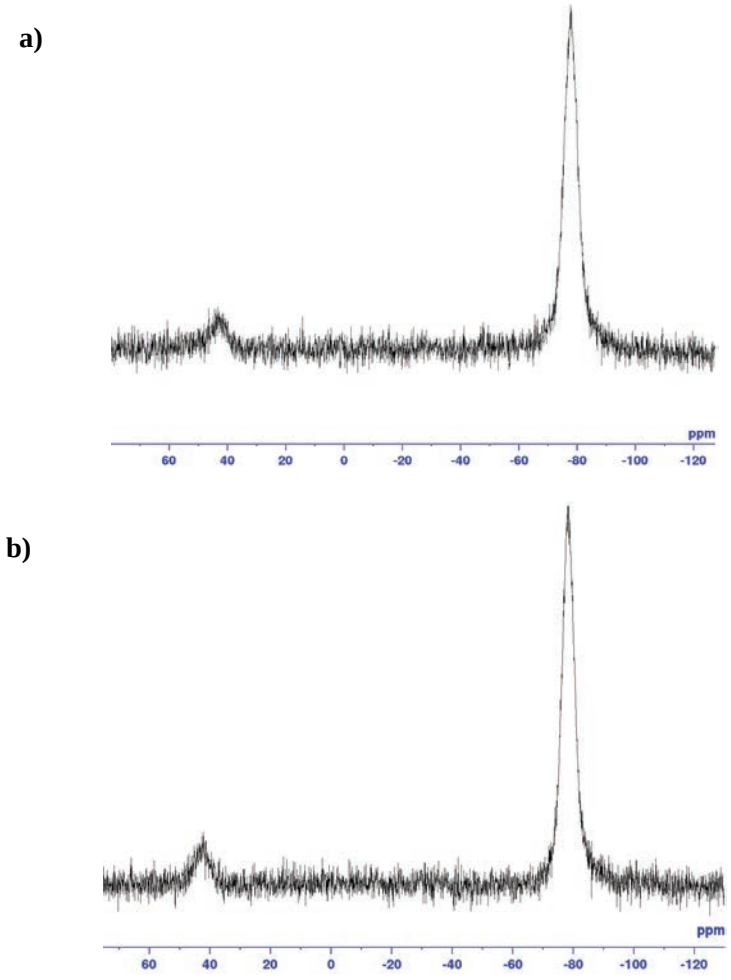

Figure S1-2. ^{51}V NMR spectra (25 ^{0}C, C_6D_6) of a) $V(CHSiMe_3)(NAd)(CH_2SiMe_3)(PMe_3)_2$ (**1**), b) **1** in the presence of PMe_3 (20 equiv).

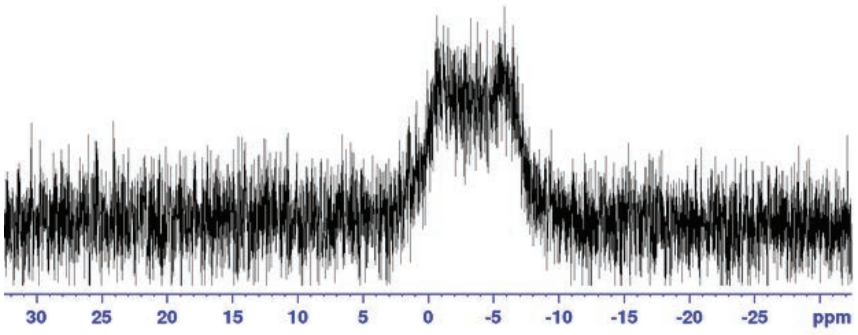

Figure S1-3. ^{31}P NMR spectrum (25 ^{0}C, C_6D_6) of $V(CHSiMe_3)(NAd)(CH_2SiMe_3)(PMe_3)_2$.

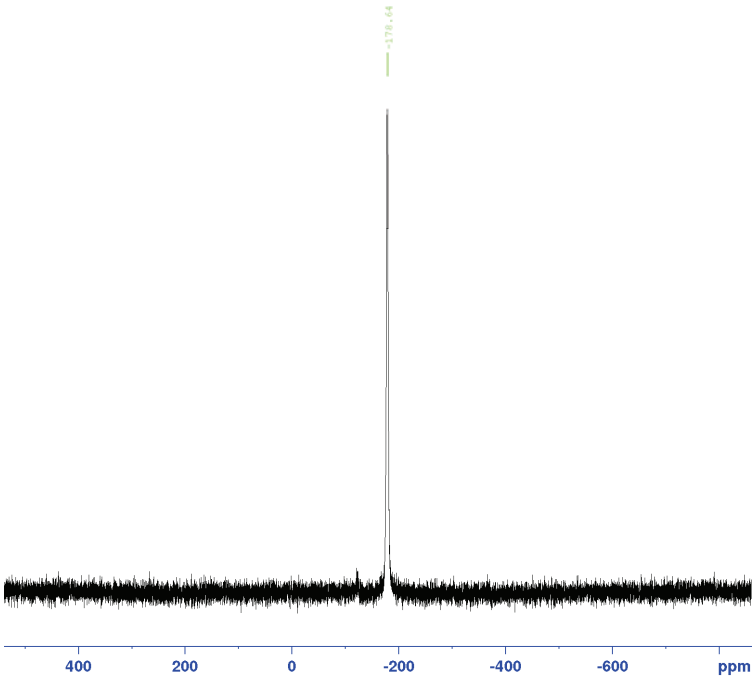

Figure S1-4. ^{51}V NMR spectra (25 ^{0}C, C_6D_6) of V(CHSiMe$_3$)(NAd)(O-2,6-Me$_2$C$_6$H$_3$)(PMe$_3$)$_2$ (**2a**).

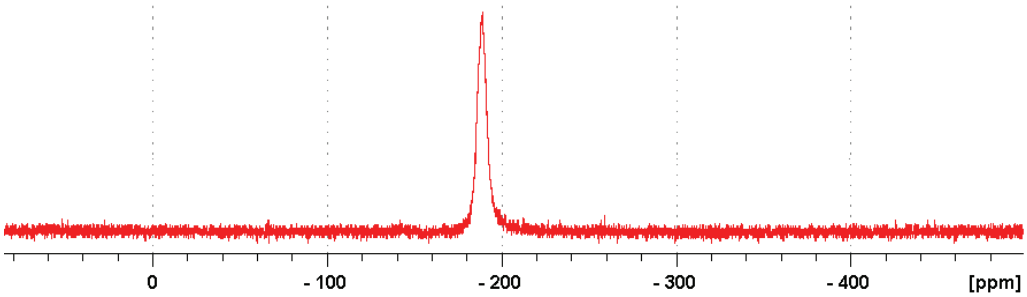

Figure S1-5. ^{51}V NMR spectrum (-25 ^{0}C, toluene-d_8) of V(CHSiMe$_3$)(NAd)(O-2,6-Me$_2$C$_6$H$_3$)(PMe$_3$)$_2$ (**2a**).

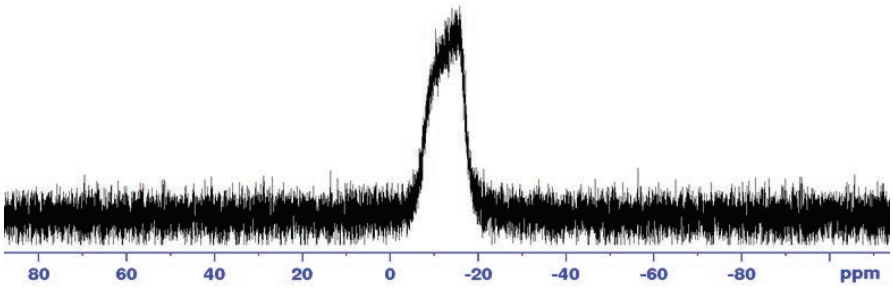

Figure S1-6. ^{31}P NMR spectra (25 ^{0}C, C_6D_6) of V(CHSiMe$_3$)(NAd)(O-2,6-Me$_2$C$_6$H$_3$)(PMe$_3$)$_2$ (**2a**).

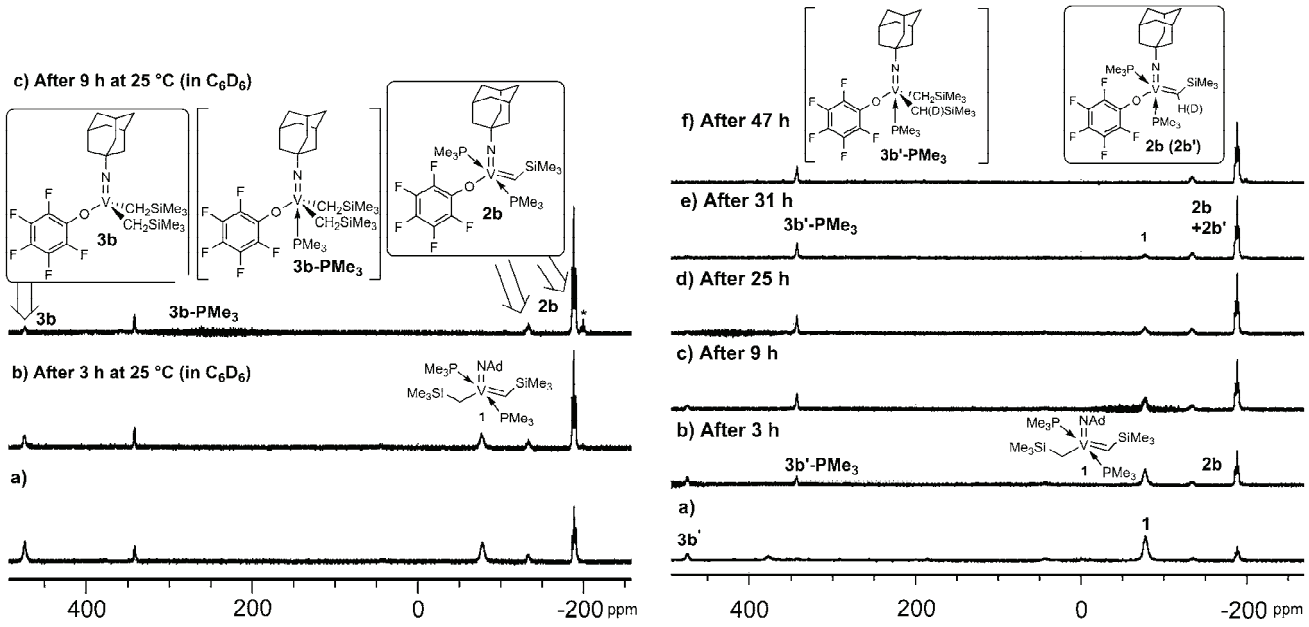

Figure S1-7. ^{51}V NMR spectra for monitoring reaction of $V(CHSiMe_3)(NAd)(CH_2SiMe_3)(PMe_3)_2$ (**1**) with C_6F_5OH (1equiv, left), C_6F_5OD (1equiv, right) in C_6D_6 at 25 ºC.

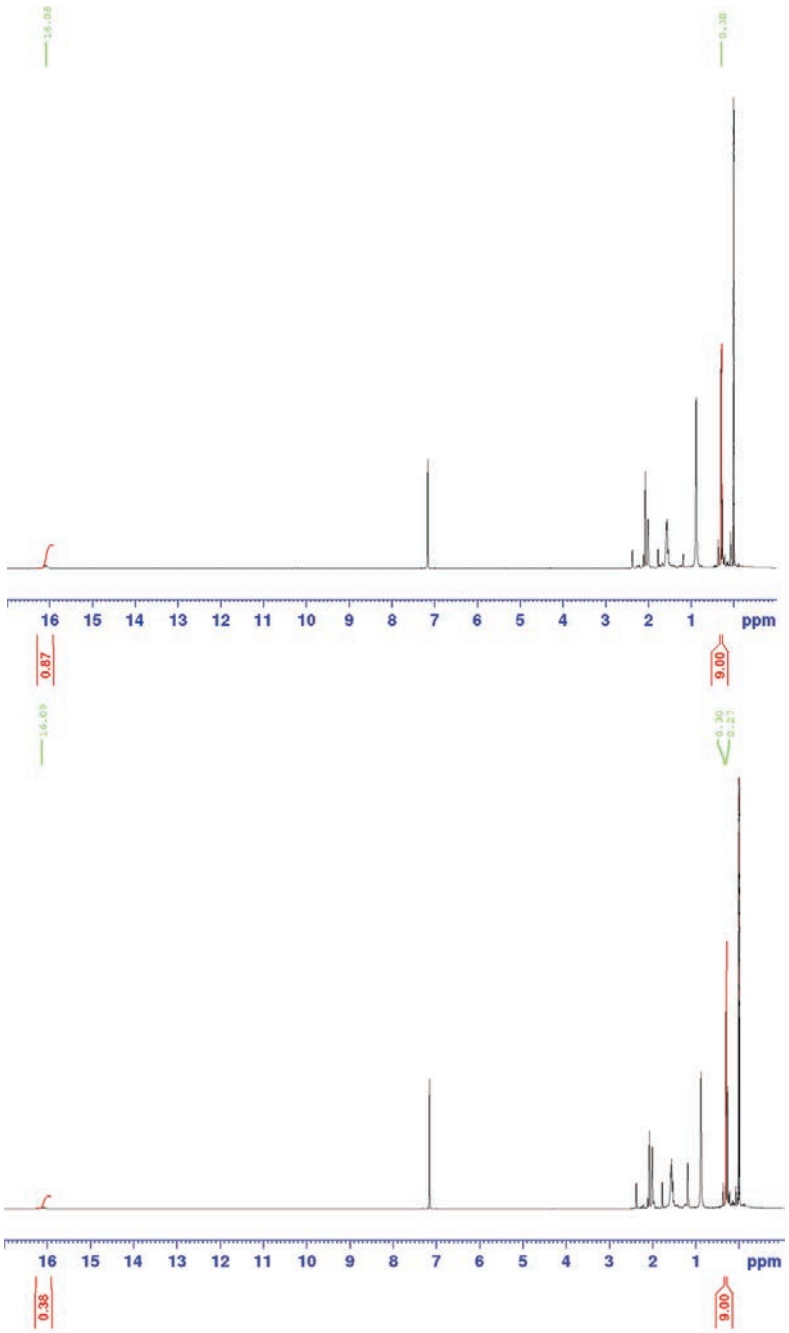

Figure S1-8. ^{1}H NMR spectra for monitoring reaction of $V(CHSiMe_3)(NAd)(CH_2SiMe_3)(PMe_3)_2$ (**1**) with C_6F_5OH (1equiv, top), C_6F_5OD (1equiv, bottom) in C_6D_6 at 25 ºC.

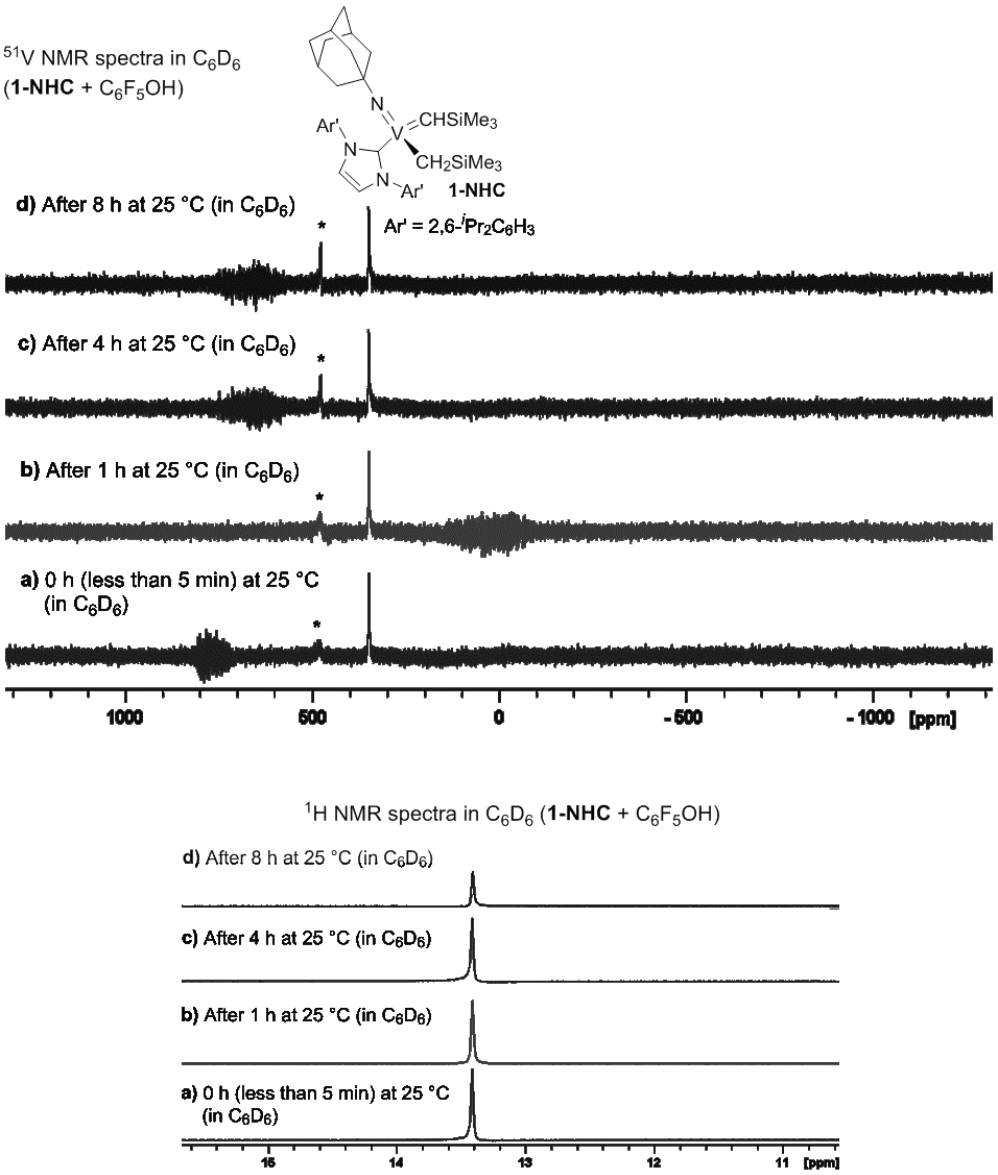

Figure S1-9. NMR spectra for monitoring reaction of V(CHSiMe$_3$)(NAd)(CH$_2$SiMe$_3$)(NHC) (**1-NHC**) with C_6F_5OH (1equiv) in C_6D_6 at 25 ºC.

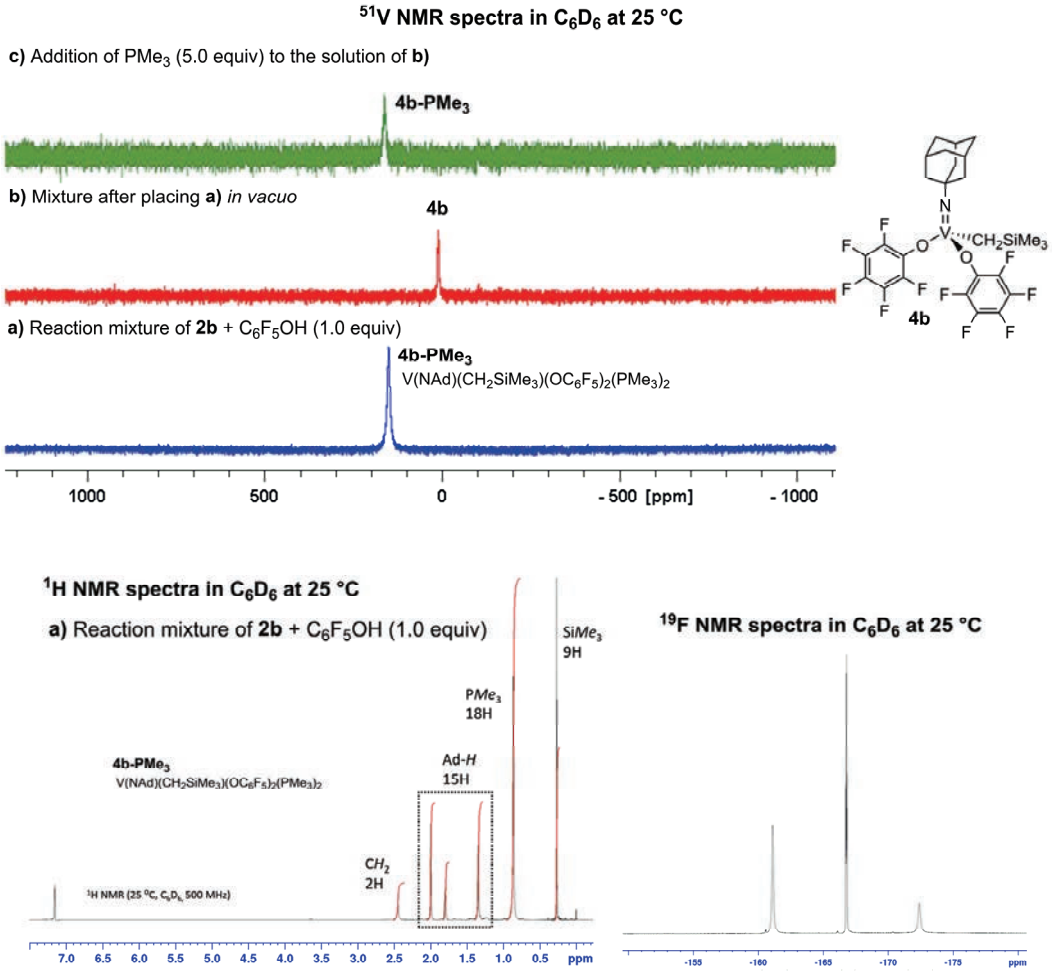

Figure S1-10. NMR spectra for reaction of $V(CHSiMe_3)(NAd)(OC_6F_5)(PMe_3)_2$ (**2b**) with C_6F_5OH (1equiv) in C_6D_6 at 25 ºC.

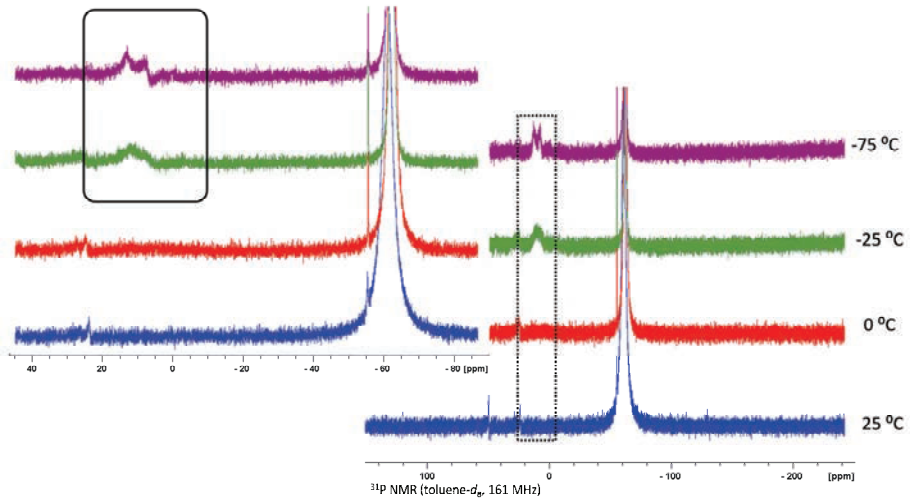

Figure S1-11. ^{31}P NMR spectra for $V(NAd)(CH_2SiMe_3)(OC_6F_5)_2$ (**4b**) in presence of PMe_3 (5.0 equiv) in toluene-d_8 at various temperature.

Table S1. Crystal and data collection parameters for $V(CHSiMe_3)(NAd)(CH_2SiMe_3)(PMe_3)_2$ (**1**, Ad = 1-adamantyl), $V(CHSiMe_3)(NAd)(O\text{-}2,6\text{-}Me_2C_6H_3)(PMe_3)_2$ (**2a**).

Complex	$V(CHSiMe_3)(NAd)(CH_2SiMe_3)(PMe_3)_2$	$V(CHSiMe_3)(NAd)(O\text{-}2,6\text{-}Me_2C_6H_3)(PMe_3)_2$
Formula; Formula weight	$C_{24}H_{54}NP_2Si_2V$; 525.76	$C_{28}H_{52}NOP_2SiV$; 559.70
Habits; Crystal size (mm)	orange, platelet; 0.440×0.370×0.010	yellow, prism; 0.320×0.300×0.200
Crystal system	triclinic	triclinic
Space group	P-1 (#2)	P-1 (#2)
a (Å); b(Å); c (Å)	10.339(3); 10.355(3); 17.415(5)	12.461(4); 13.957(5); 19.235(5)
β(deg); V ($Å^3$)	101.373(7); 1690.1(9)	90.355(6); 3204(2)
Z value	2	4
D_{calcd} (g/cm^3)	1.033	1.160
F_{000}	572.00	1208
Temp (K)	-180	0
λ (Mo Kα) (Å)	0.71075	0.71075
No. of reflections measured: (R_{int})	Total: 17839, Unique: 7765	Total: 32271, Unique: 14537
No.of observations (I > 3.00σ(I))	7765	14537
No. of variables	284	621
Residuals: R1 ;Rw	0.0598; 0.1813	0.0848; 0.2319
GOF	1.092	0.947
Max (minimum) peak in final diff. map (e-/ $Å^3$)	0.75	1.42