Binary Role of an Ylide in Formation of a Terminal Methylidene Complex of Niobium

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Supporting Information

Experimental Details

General procedures: Unless otherwise stated, all operations were performed in a M. Braun Lab Master double-dry box under an atmosphere of purified nitrogen or using high vacuum standard Schlenk techniques under a nitrogen atmosphere. Anhydrous benzene, pentane, and toluene were purchased from Aldrich in sure-sealed reservoirs (18 L) and dried by passage through two columns of activated alumina and a Q-5 column. THF and Et_2O were distilled, under nitrogen, from purple sodium benzophenone ketyl and stored over sodium metal. Distilled THF and Et_2O were transferred under vacuum into thick walled reaction vessels before being carried into a dry box. Deuterobenzene was purchased from Cambridge Isotope Laboratory (CIL), degassed by freeze-pump-thaw cycles and stored over 4 Å molecular sieves. Celite, alumina, and 4 Å molecular sieves were activated under vacuum overnight at 200 ºC. Compounds NaOAr' (Ar' = 2,6-$CHPh_2)_2$-4-^{t}Bu-C_6H_2),[1] H_2CPPh_3,[2] and $HCPh(SO_2CF_3)_2$[3] were prepared following the literature procedures. $Nb(CH_3)_2Cl_3$[4] was prepared according to a previously reported synthesis but, we have found this complex is sensitive to incandescent light resulting in the formation of an insoluble brown solid. Thus, the synthesis and subsequent reactions involving $Nb(CH_3)_2Cl_3$ should be performed in the absence of light. All other chemicals were purchased from Strem Chemicals, Aldrich, Alfa Aesar, or Matrix Scientific and used as received. ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on Varian 500 or 400 MHz NMR spectrometers. ^{1}H and ^{13}C NMR spectra are reported with reference to residual ^{1}H solvent resonances of C_6D_6 at 7.16 and 128.06 ppm, respectively. ^{19}F and ^{31}P NMR spectra are reported with respect to external CF_3CO_2H (-78.5 ppm) and H_3PO_4 (aqueous solution, 0.0 ppm). Elemental analyses were performed at Robertson Microlit Laboratories.

Synthesis of [(Ar'O)$_2$Nb(CH$_3$)$_2$Cl] (1). In the absence of light a 250 mL round bottom flask containing a 40 mL orange benzene solution of Nb(CH$_3$)$_2$Cl$_3$ (0.401 g, 1.744 mmol) was added dropwise an opaque white 100 mL benzene solution of Na(OAr')(THF) (2.012 g, 3.489 mmol) via a glass pipette, resulting in a gradual color change to yellow-brown with the precipitation of a brownish-white solid. After stirring for 12 hours at room temperature the reaction mixture was filtered through a celite plug and a yellow colored filtrate was obtained. The filtrate was concentrated to approximately 5 mL and transferred to a 20 mL scintillation vial. To the 5mL benzene solution was added 15 mL of pentane. After vigorous stirring for approximately 30 minutes yellow solid had begun to precipitate from the solution. The resulting suspension was filtered through a medium porosity glass frit and the resulting yellow solid was rinsed with 10 mL of cold pentane (-37 °C). Yellow single crystals of **1** were obtained by slow diffusion of pentane into concentrated benzene solution at room temperature. Yield = 72% (1.409 g, 1.256 mmol). **^{1}H NMR (25 °C, 400.11 MHz, C$_6$D$_6$):** δ 7.22 (m, 20H, -Ar-*H*$_{ortho}$/-Ar-*H*$_{meta}$), 7.07 (t, J_{HH} = 7.47 Hz, 16H, -Ar-*H*$_{meta}$), 6.99 (t, J_{HH} = 7.30 Hz, 8H, -Ar-*H*$_{para}$), 6.62 (s, 4H, -C*H*(Ph)$_2$), 1.03 (s, 6H, Nb-C*H*$_3$), 1.04 (s, 18H, -C(C*H*$_3$)$_3$). **^{13}C {^{1}H} NMR (25 °C, 100.61 MHz, C$_6$D$_6$):** δ 157.29 (-*C*$_{Ar}$), 145.90 (-*C*$_{Ar}$), 144.84 (-*C*$_{Ar}$), 134.88 (-*C*$_{Ar}$), 130.33 (-*C*H$_{Ar}$), 128.63 (-*C*H$_{Ar}$), 128.59 (-*C*H$_{Ar}$), 126.68 (-*C*H$_{Ar}$), 62.06 (-*C*H$_3$), 50.47 (-*C*H(Ph)$_2$), 34.59 (-*C*(CH$_3$)$_3$), 31.24 (-C(*C*H$_3$)$_3$). **Anal. Calcd. For [((OAr')$_2$Nb(CH$_3$)$_2$Cl)·(toluene)], C$_{81}$H$_{80}$ClNbO$_2$:** C, 80.15; H, 6.64. **Found:** C, 80.49; H, 6.83.

** To obtain complex **2** in pure form, the Nb(CH$_3$)$_2$Cl$_3$ (^{1}H NMR (25 °C, 400.11 MHz, C$_6$D$_6$): δ 2.31 ppm) starting material must not contain any amount of Nb(CH$_3$)Cl$_4$ (^{1}H NMR (25 °C, 400.11 MHz, C$_6$D$_6$): δ 2.56 ppm). Performing the reaction with impure starting material results in a mixture of products which we speculate to be complex **2** and [(Ar'O)$_2$Nb(CH$_3$)Cl$_2$]. Unfortunately similar solubility has prevented the separation and characterization of the later. **

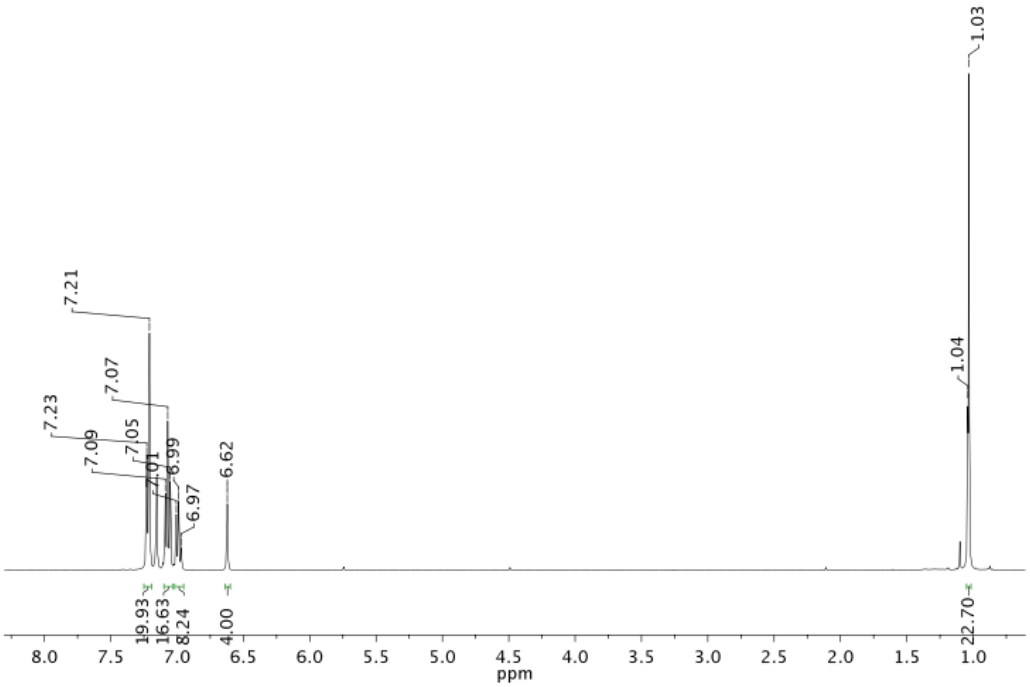

Figure S1. ^{1}H NMR spectrum of **1** recorded in C_6D_6 (400.11 MHz, 25°C).

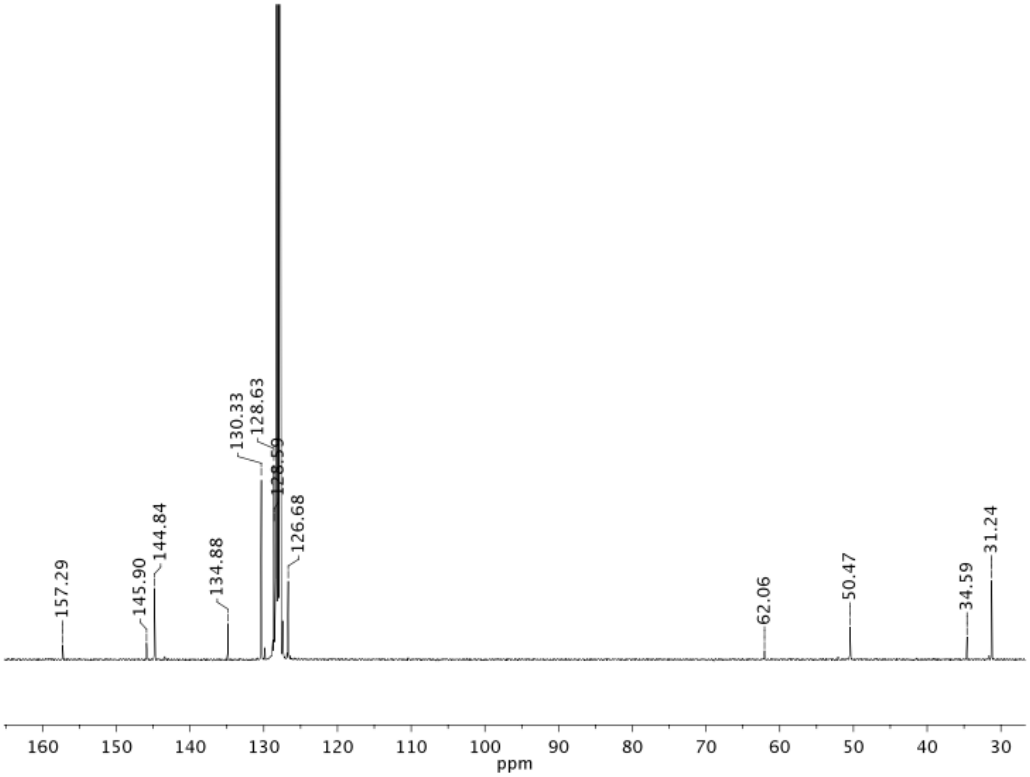

Figure S2. ^{13}C {^{1}H} NMR spectrum of **1** recorded in C_6D_6 (100.61 MHz, 25°C).

Synthesis of [(Ar'O)$_2$Nb=CH$_2$(CH$_3$)(H$_2$CPPh$_3$)] (2). At -78 °C a 20 mL scintillation vial containing a 10 mL yellow toluene solution of **1** (410 mg, 0.366 mmol) was added dropwise a yellow 5 mL toluene solution of H_2CPPh_3 (202 mg, 0.731 mmol) via a glass pipette, resulting in a slight darkening of the reaction mixture. The reaction mixture was allowed to stir overnight, allowing the solution to gradually warm to room temperature. After stirring for 12 hours, a white precipitate had formed which was accompanied by a color change to bright orange. The reaction mixture was subsequently filtered through a medium porosity glass frit containing celite. The resulting orange filtrate was reduced in volume to approximately 3 mL and 10 mL of pentane was added, precipitating orange microcrystalline solid. After storing the suspension at -37 °C for 12 hours, the orange microcrystalline solid was isolated on a medium porosity glass frit and rinsed with 5 mL of cold pentane (-37 °C). Orange-red single crystals of **2** were grown from a concentrated toluene solution layered with pentane stored at -37 °C. Yield = 87% (0.432 g, 0.317 mmol). **^{1}H NMR (25 °C, 500.39 MHz, C$_6$D$_6$):** δ 9.94 (d, $^4J_{HP}$ = 1.35 Hz, 2H, Nb=C*H*$_2$), 7.78 (br m, 4H, -Ar-*H*), 7.48 (br m, 10H -Ar-*H*), 7.30 (br m, 10H, -Ar-*H*, -C*H*(Ph)$_2$), 7.20 (br m, -Ar-*H*), 7.11 (br m, -Ar-*H*), 7.04 (dd, J_{HH} = 7.45 Hz, $^3J_{HP}$ = 12.03 Hz, 6H, -Ar-*H*$_{ortho}$, m, 10H, -Ar-*H*), 6.90 (t, J_{HH} = 7.45 Hz, 3H, -Ar-*H*$_{para}$), 6.78 (br m, 4H, -Ar-*H*), 6.67 (br m, 2H, -Ar-*H*), 6.62 (td, J_{HH} = 7.97 Hz, $^4J_{HP}$ = 2.69 Hz, 6H, -Ar-*H*$_{meta}$), 6.49 (br m, 2H, -C*H*(Ph)$_2$), 1.08 (s, 18H, -C(C*H*$_3$)$_3$), 0.96 (s, 3H, Nb-C*H*$_3$) 0.67 (d, $^2J_{HP}$ = 17.12 Hz, 2H, -C*H*$_2$PPh$_3$). **^{13}C {^{1}H} NMR (25 °C, 100.61 MHz, C$_6$D$_6$):** δ 230.64 (d, $^3J_{CP}$ = 6.58 Hz, $^1J_{CH}$ = 139 Hz, Nb=*C*H$_2$), 158.23 (s, -*C*$_{Ar}$), 147.27 (br s, *C*$_{Ar}$), 146.93 (br s, -*C*$_{Ar}$), 146.38 (br s, -*C*$_{Ar}$), 145.08 (br s, -*C*$_{Ar}$), 142.67 (s, -*C*$_{Ar}$), 133.29 (d, J_{CP} = 8.75 Hz, -*C*$_{Ar}$), 131.92 (s, -*C*$_{Ar}$), 131.86 (d, J_{CP} = 2.5 Hz, -*C*$_{Ar}$), 130.90 (br s, -*C*$_{Ar}$), 130.79 (br s, -*C*$_{Ar}$), 130.48 (br s, -*C*$_{Ar}$), 128.61 (s, -*C*$_{Ar}$), 126.42 (br s, -*C*$_{Ar}$), 126.12 (s, -*C*$_{Ar}$), 125.89 (br s, -*C*$_{Ar}$) 52.14 (s, -*C*H(Ph)$_2$), 48.89 (s, -*C*H(Ph)$_2$), 34.42 (s, -*C*(CH$_3$)$_3$), 31.51 (s, -C(*C*H$_3$)$_3$), 30.55 (s, -*C*H$_3$), 10.53 (d, J_{CP} = 26.25 Hz, -*C*H$_2$P(Ph)$_3$). **^{31}P {^{1}H} NMR (25 °C, 162.0 MHz, C$_6$D$_6$):** δ 34.47 (s). **Anal. Calcd. For C$_{93}$H$_{88}$NbO$_2$P:** C, 82.04; H, 6.51. **Found:** C, 82.18; H, 6.74.

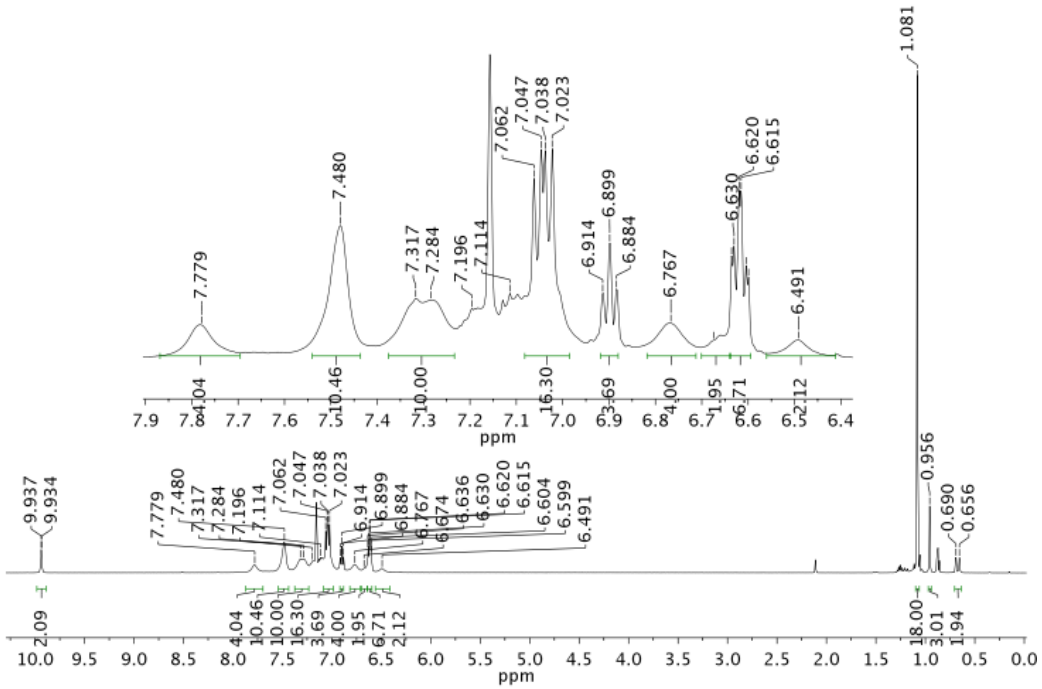

Figure S3. ^{1}H NMR spectrum of **2** recorded in C_6D_6 (500.39 MHz, 25°C).

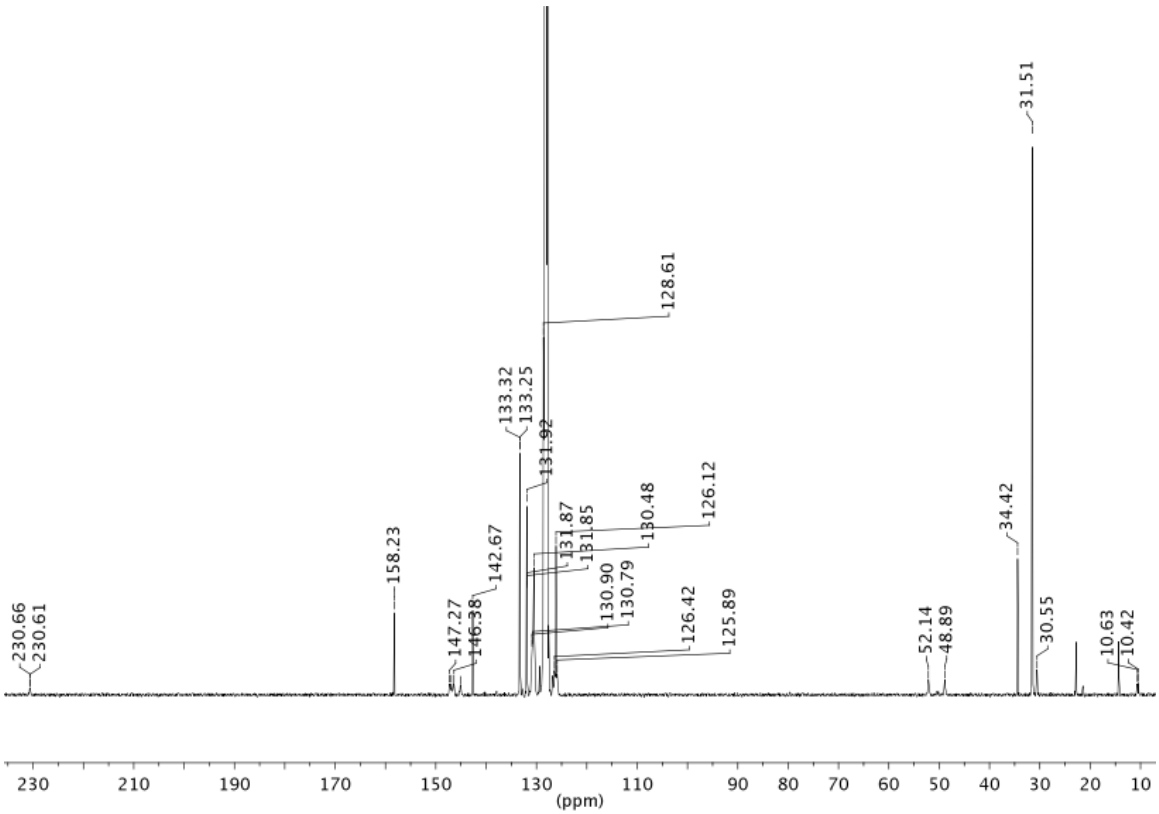

Figure S4. ^{13}C {^{1}H} NMR spectrum of **2** recorded in C_6D_6 (125 MHz, 25°C).

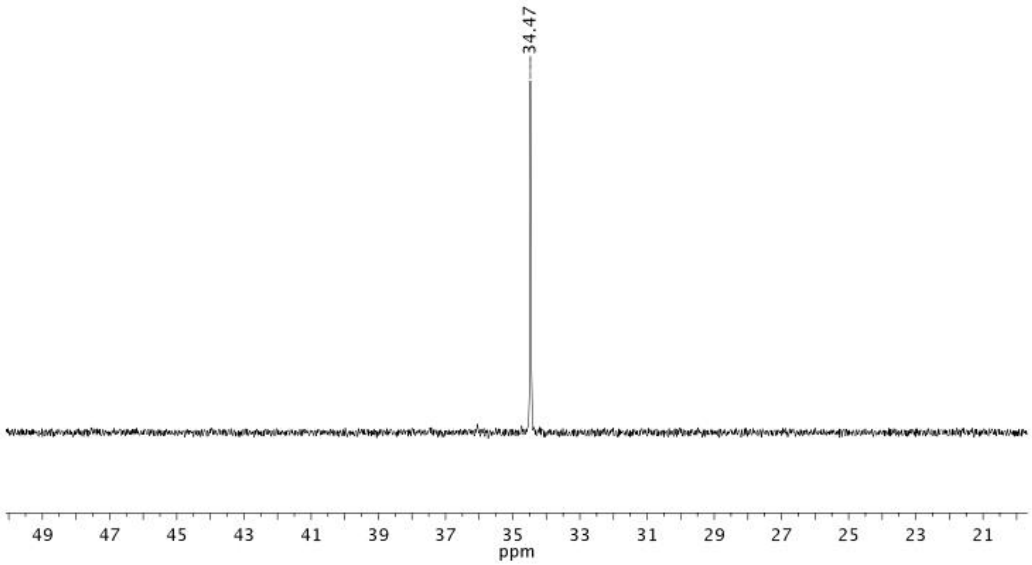

Figure S5. ^{31}P $\{^{1}H\}$ NMR spectrum of **2** recorded in C_6D_6 (162.0 MHz, 25°C).

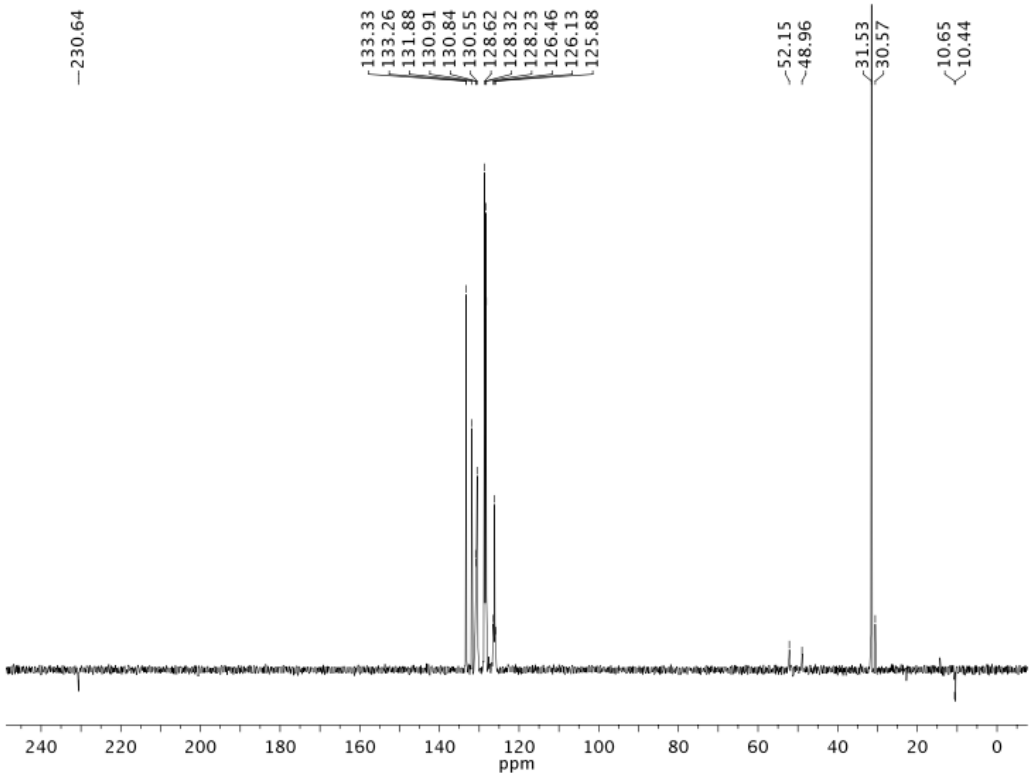

Figure S6. DEPT-135 NMR spectrum of **2** recorded in C_6D_6 (500 MHz, 25°C).

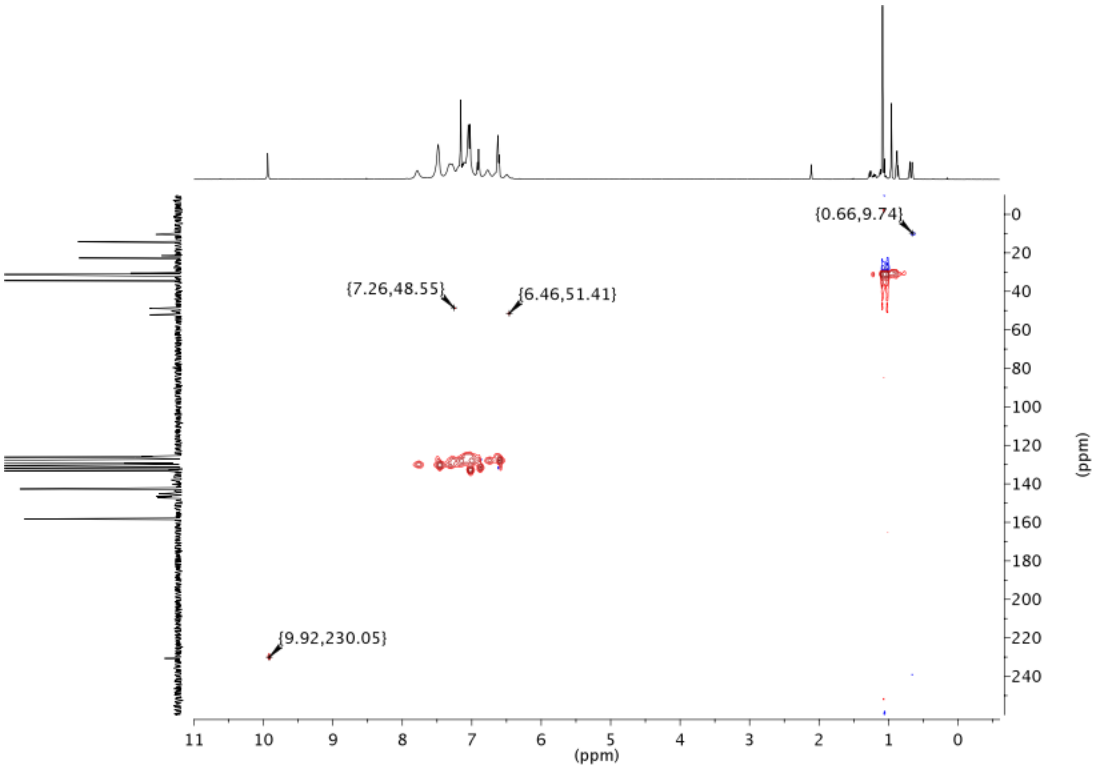

Figure S7. $^{13}C\{^{1}H\}$-^{1}H HSQC NMR spectrum of **2** recorded in C_6D_6 (500 MHz, 25°C). Only selected chemical shifts are labeled.

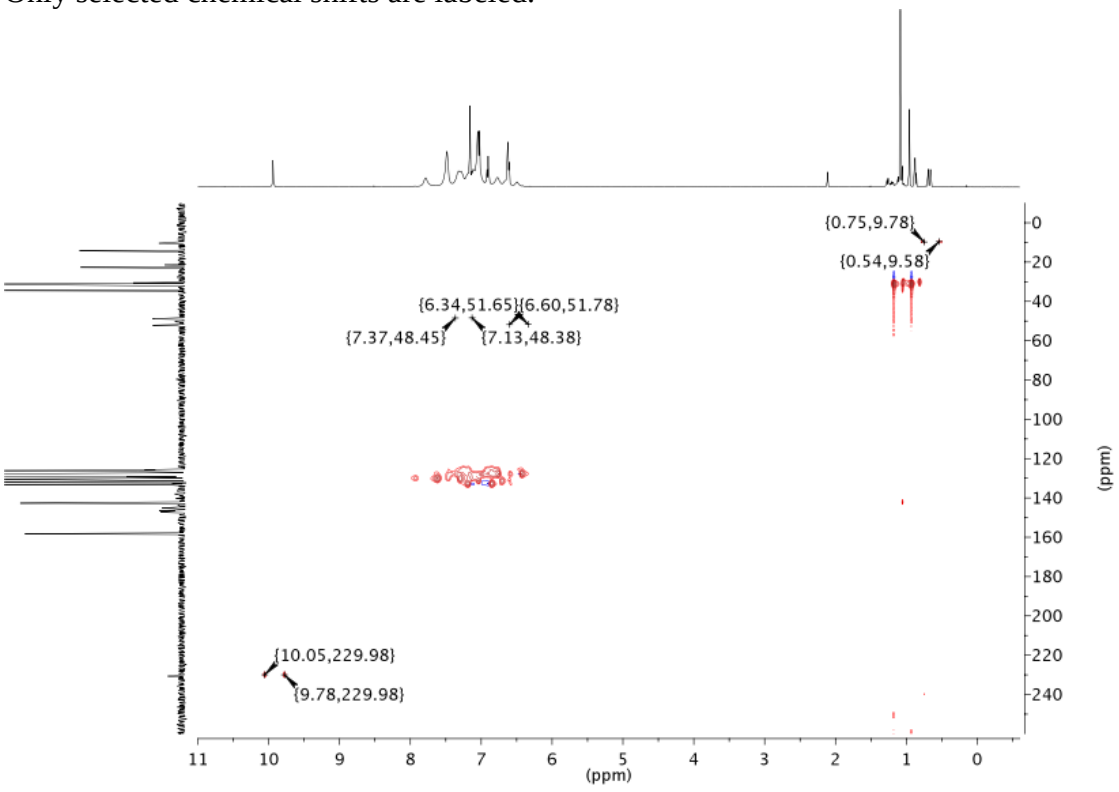

Figure S8. ^{13}C-^{1}H HSQC NMR spectrum of **2** recorded in C_6D_6 (500 MHz, 25°C). Only selected chemical shifts are labeled.

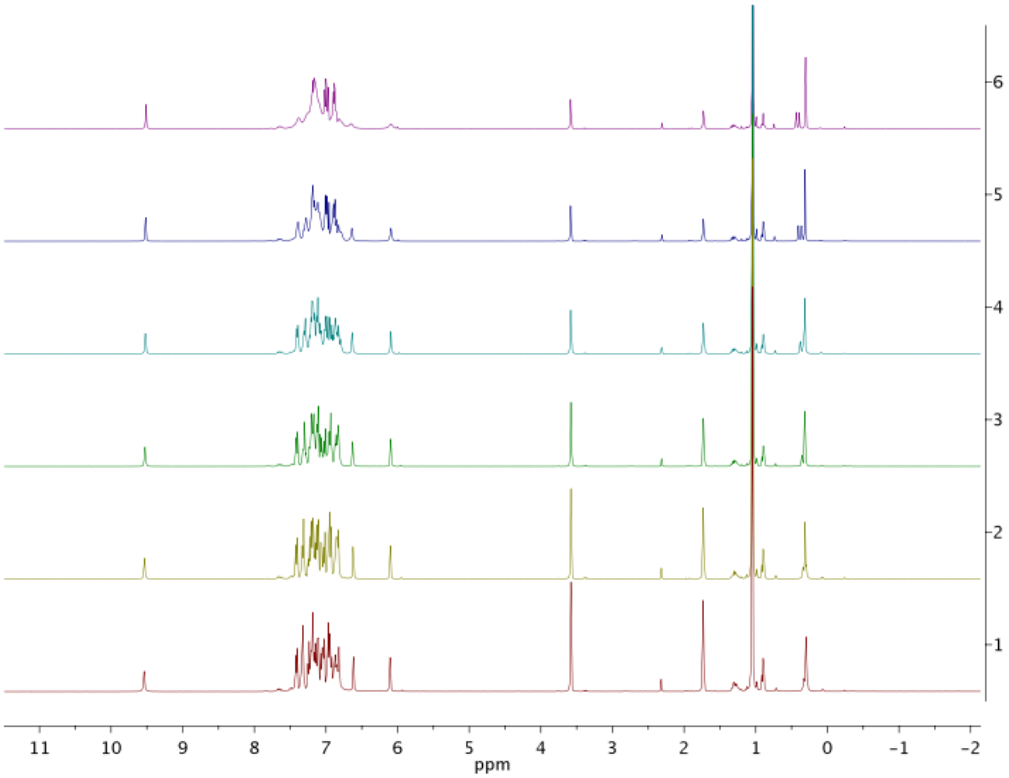

Figure S9. Variable temperature ^{1}H NMR spectra of **2** recorded in THF-D_8 in 15° intervals ranging -55°C (bottom) to 20°(top).

Synthesis of [(Ar'O)$_2$Nb=O(CH$_3$)(H$_2$CPPh$_3$)] (3). To a 20 mL scintillation vial containing a 10 mL orange toluene solution of **2** (181 mg, 0.133 mmol) was added dropwise a clear 5 ml toluene solution of benzophenone (24 mg, 0.132 mmol) via a glass pipette, resulting in no immediate color change. The solution gradually turned yellow in color over the duration of 4 hours and to ensure complete conversion the reaction was allowed to proceed overnight. The resulting yellow solution was filtered through a glass pipette containing a plug of celite. All volatiles were subsequently removed from the yellow solution resulting in the isolation of a yellow colored solid. Removal of 1,1-diphenylethylene from the yellow solid was accomplished by rinsing with approximately 10 mL of Et_2O on a medium porosity glass frit, resulting in pure product. Yellow single crystals of **3** were obtained by layering a concentrated benzene solution with pentane at room temperature. Yield = 79% (0.143 g, 0.105 mmol). **^{1}H NMR (25 °C, 400.11 MHz, C$_6$D$_6$):** δ 7.78 (br m, 4H, -Ar-*H*), 7.54 (br m, 6H, -Ar-*H*), 7.43 (br m, 4H, -Ar-*H*), 7.27 (br m, 14H, -Ar-*H*, -C*H*(Ph)$_2$), 7.11 (dd, J_{HH} = 7.60 Hz, $^3J_{HP}$ = 12.13 Hz, 6H, -Ar-H_{ortho}), 6.91 (t, J_{HH} = 7.32 Hz, 3H, -Ar-H_{para}), 6.76 (br m, 4H, -Ar-*H*), 6.66 (td, J_{HH} = 7.57 Hz, $^4J_{HP}$ = 5.29 Hz, 6H, -Ar-H_{meta}), 6.61 (br m, -Ar-*H*), 6.42 (br m, 2H, -C*H*(Ph)$_2$), 1.12 (s, 18H, -C(C*H*$_3$)$_3$), 1.00 (d, $^2J_{HP}$ = 18.62 Hz, 2H, -C*H*$_2$PPh$_3$), 0.73 (s, 3H, Nb-C*H*$_3$). **^{13}C {^{1}H} NMR (25 °C, 100.61 MHz, C$_6$D$_6$):** δ 158.99 (br s, -*C*$_{Ar}$), 147.00 (br s, -*C*$_{Ar}$), 146.56 (br s, *C*$_{Ar}$), 146.23 (br s, -*C*$_{Ar}$), 145.57 (br s, -*C*$_{Ar}$), 142.25 (s, -*C*$_{Ar}$), 133.32 (d, J_{CP} = 10.01 Hz, -*C*$_{Ar}$), 132.66 (d, J_{CP} = 2.44 Hz, -*C*$_{Ar}$), 130.78 (s, -*C*$_{Ar}$), 130.45 (br s, -*C*$_{Ar}$), 130.31 (br s, -*C*$_{Ar}$), 128.82 (s, -*C*$_{Ar}$), 128.72 (s, -*C*$_{Ar}$), 126.26 (s, -*C*$_{Ar}$), 126.09 (br s, -*C*$_{Ar}$), 125.93 (br s, -*C*$_{Ar}$), 125.79 (br s, -*C*$_{Ar}$), 125.58 (s, -*C*$_{Ar}$) 51.96 (s, -*C*H(Ph)$_2$), 49.06 (s, -*C*H(Ph)$_2$), 34.43 (s, -*C*(CH$_3$)$_3$), 31.84 (s, -*C*H$_3$), 31.58 (s, -C(*C*H$_3$)$_3$), 14.72 (d, J_{CP} = 30.23 Hz, -*C*H$_2$P(Ph)$_3$). **^{31}P {^{1}H} NMR (25 °C, 162.0 MHz, C$_6$D$_6$):** δ 33.85 (s).

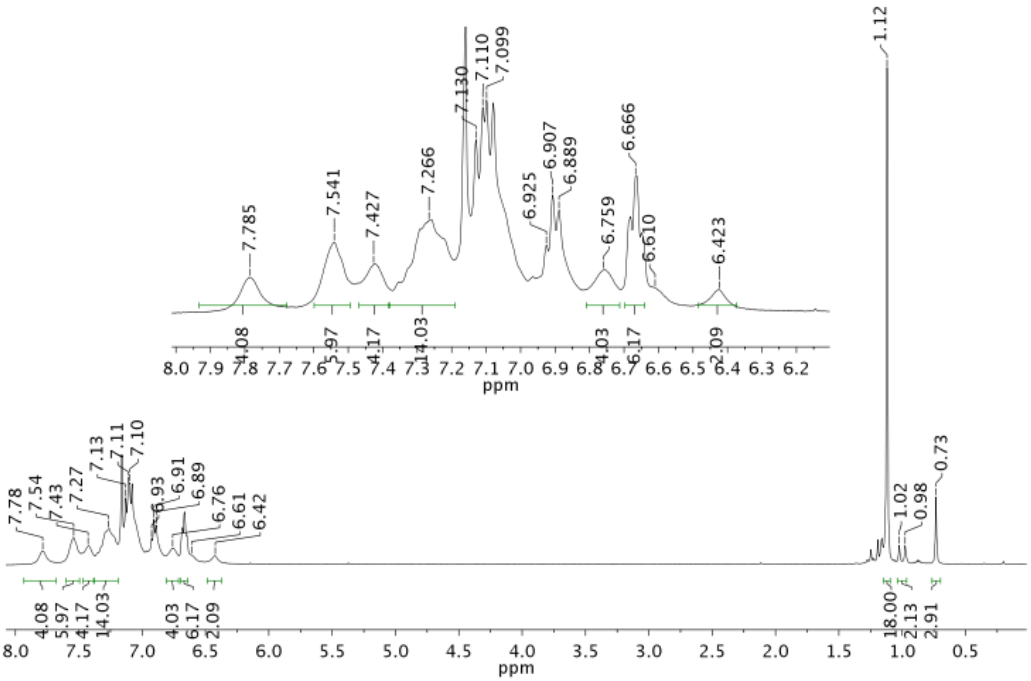

Figure S10. ^{1}H NMR spectrum of **3** recorded in C_6D_6 (400.11 MHz, 25°C).

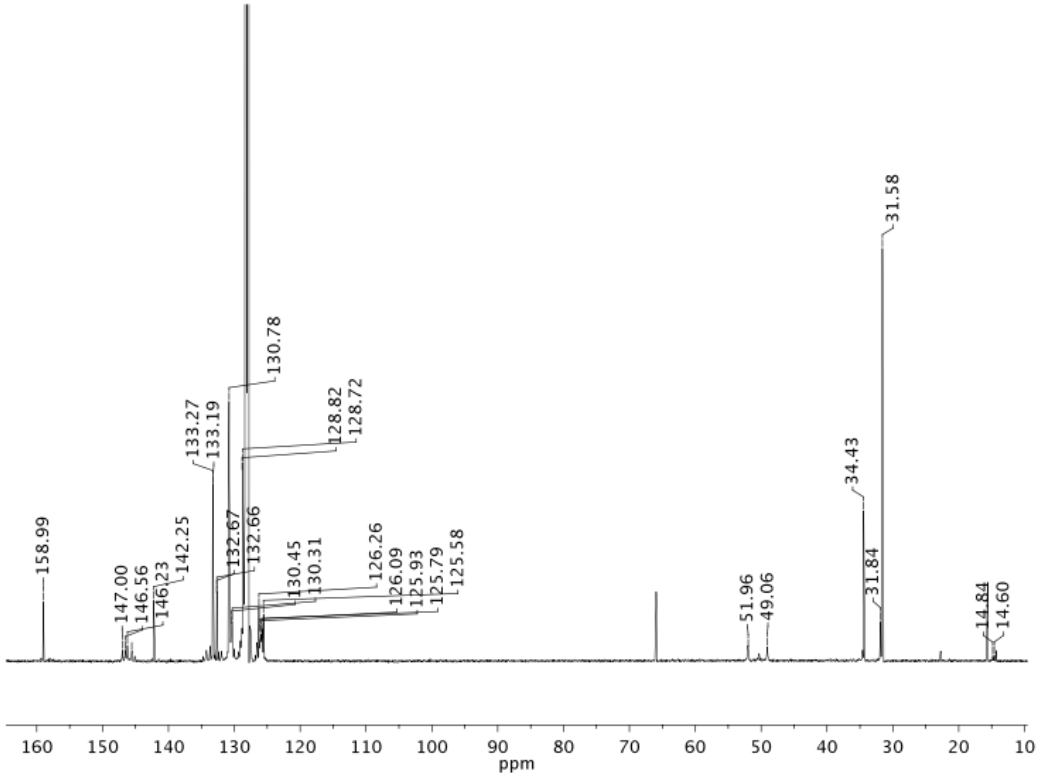

Figure S11. ^{13}C {^{1}H} NMR spectrum of **3** recorded in C_6D_6 (125 MHz, 25°C).

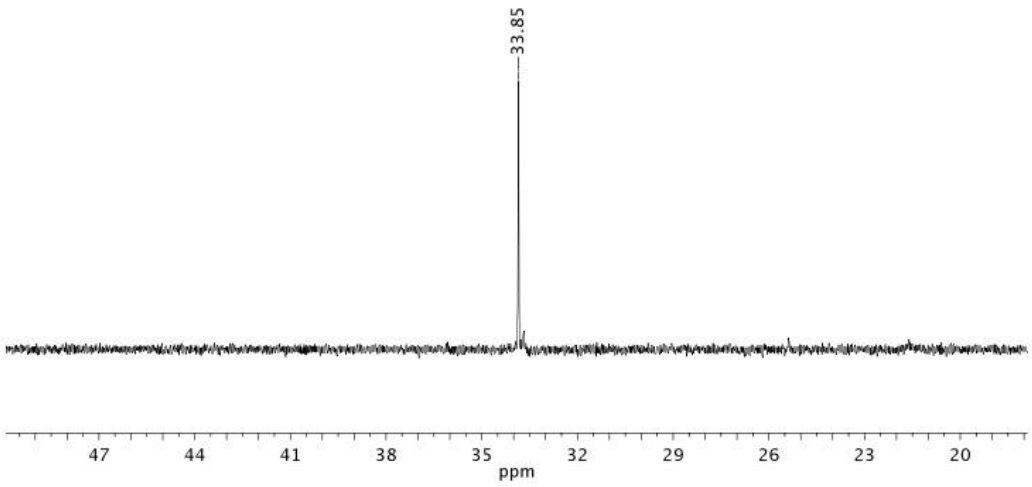

Figure S12. ^{31}P $\{^{1}H\}$ NMR spectrum of **3** recorded in C_6D_6 (162.0 MHz, 25°C).

Synthesis of $[(Ar'O)_2Nb(CH_3)_2(H_2CPPh_3)][CPh(SO_2CF_3)_2]$ (4). To a 20 mL scintillation vial a 5 mL orange toluene solution of **2** (44 mg, 0.033 mmol) was added dropwise a clear 2 mL toluene solution of $HCPh(SO_2CF_3)_2$ (12 mg, 0.037 mmol) resulting in an immediate color change to yellow. After allowing the reaction to precede for 30 min the reaction mixture was filtered through a pipet containing a celite plug. All volatiles were removed from the yellow filtrate yielding a yellow oil. Addition of 6 ml of a 5:1 pentane/benzene mixture with vigorous stirring resulted in the precipitation of yellow solid. After stirring for approximately 10 minutes the filtrate was removed using a glass pipet and the resulting yellow solid dried under reduced pressure. Yellow-orange single crystals of **4** were grown rapidly at -37 °C by layering a concentrated toluene solution containing several drops of benzene with pentane. Yield = 55% (0.031 g, 0.018 mmol). **^{1}H NMR (25 °C, 400.11 MHz, C_6D_6):** δ8.01 (d, $^2J_{HP}$ = 7.47 Hz, 2H, -Ar-H_{ortho}), 7.25 (br m, -Ar-*H*), 7.19 (br, -Ar-*H*), 7.17 (br, -Ar-*H*), 7.13 (br m, -Ar-*H*), 7.08 (br, -Ar-*H*), 7.05 (br m, -Ar-*H*), 6.79 (br, -Ar-*H*), 5.86 (s, 4H, -C*H*$(Ph)_2$), 2.04 (d, $^2J_{HP}$ = 18.16 Hz, 2H, -CH_2PPh_3), 1.41 (br s, 6H, -CH_3), 1.00 (s, 18H, -C(CH_3)$_3$). **^{31}P {^{1}H} NMR (25 °C, 162.0 MHz, C_6D_6):** δ 27.87 (s). **^{19}F NMR (25 °C, 282.3 MHz, C_6D_6):** δ 77.54 (s). The instability of complex **4** in solution has prevented the acquisition of clean NMR spectroscopic data. Unknown impurities which are present in the NMR spectra are labeled by *.

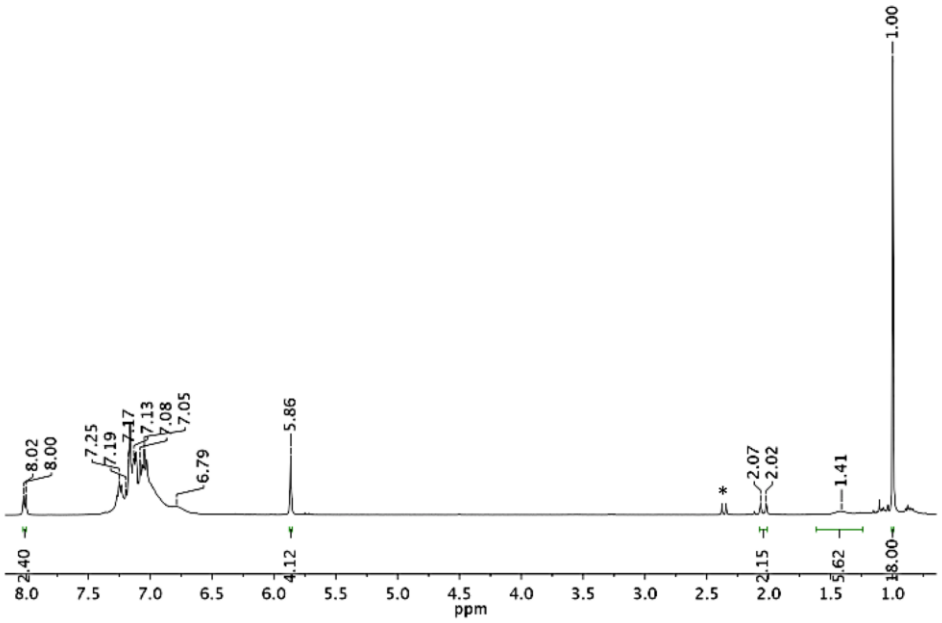

Figure S13. ^{1}H NMR spectrum of **4** recorded in C_6D_6 (400.11 MHz, 25°C). Unknown impurity is marked by *.

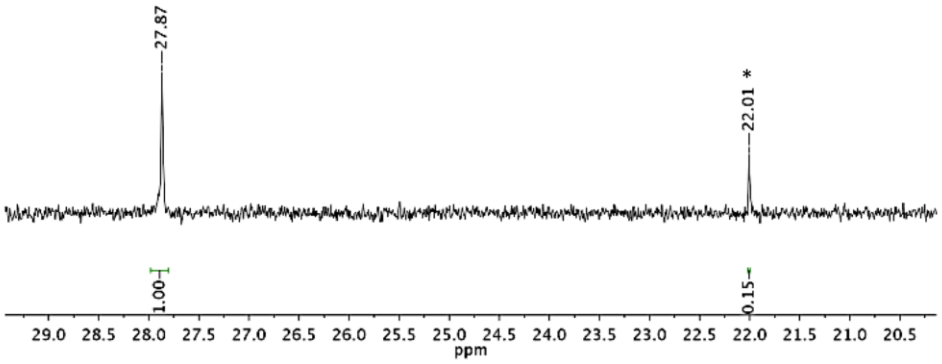

Figure S14. ^{31}P {^{1}H} NMR spectrum of **4** recorded in C_6D_6 (162.0 MHz, 25°C). Unknown impurity is marked by *.

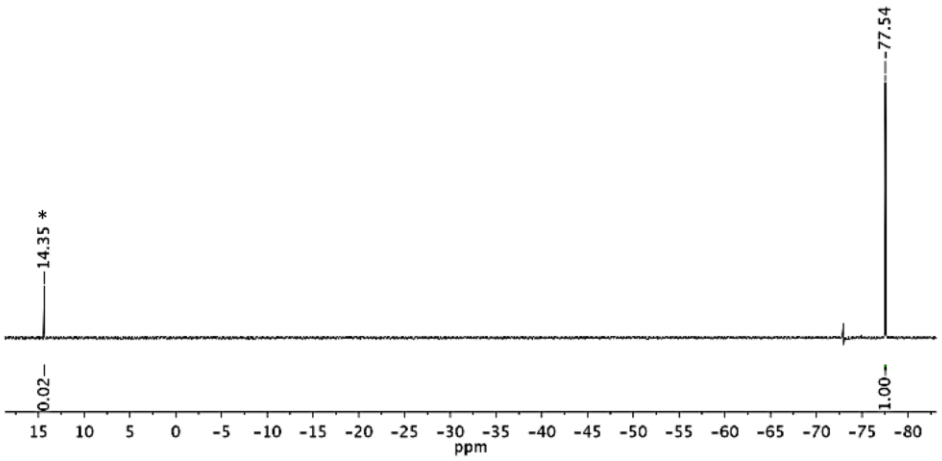

Figure S15. ^{19}F NMR spectrum of **4** recorded in C_6D_6 (282.3 MHz, 25°C). Unknown impurity is marked by *.

Crystallographic Details

Suitable crystals for analysis of **1-4** were placed onto the tip of MiTeGen loop coated in NVH oil and mounted on an Apex Kappa Duo diffractometer. The data collection was carried out at 150 K using Mo Kα radiation (graphite monochromator). A randomly oriented region of reciprocal space was surveyed to achieve complete data with a redundancy of 4. Sections of frames were collected with 0.50º steps in ω and ϕ scans. Final cell constants were calculated from the xyz centroids of a particular number of strong reflections for each crystal from the actual data collection after integration (SAINT).[5] The intensity data were corrected for absorption (SADABS).[6] The space groups were determined based on intensity statistics and systematic absences. The structures were solved using SIR-92[7] and refined (full-matrix-least squares) using either SHELXL-97[8] or Oxford University Crystals for Windows system.[9] A direct-methods solution was calculated, which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms.

Table S1. Crystallographic Parameters for Complexes 1-4

	1	**2**	**3**	**4**
molecular formula	$C_{86}H_{84}ClNbO_2$	$C_{93}H_{88}NbO_2P$	$C_{110}H_{104.50}NbO_3P$	$C_{117}H_{109}F_6NbO_6PS_2$
formula weight	1277.97	1361.60	1598.43	1913.15
temp (K)	150	150	150	150
crystal system	orthorhombic	monoclinic	monoclinic	triclinic
space group	*Pbcn*	*P2₁/n*	*P2₁*	*P-1*
cell constants				
a (Å)	24.1726(15)	14.5834(4)	14.8662(16)	15.1935(9)
b (Å)	13.1471(8)	23.9170(6)	39.237(4)	17.4577(10)
c (Å)	21.9126(12)	22.1106(5)	15.5681(16)	20.9931(12)
α (deg)	90	90	90	96.128(3)
β (deg)	90	103.7600(10)	102.424(5)	98.445(3)
γ (deg)	90	90	90	113.251(3)
Z	4	4	4	2
V (Å^3)	6963.8(7)	7490.7(3)	8868.3(16)	4976.8(5)
abs coeff (mm^{-1})	0.259	0.231	0.206	0.246
calcd density (g/cm^3)	1.219	1.207	1.197	1.277
F(000)	2696	2872	3378	2002
crystal dimensions (mm)	0.20 x 0.20 x 0.30	0.19 x 0.54 x 0.57	0.10 x 0.31 x 0.46	0.06 x 0.49 x 0.49
wavelength (Å)	0.71073	0.71073	0.71073	0.71073
h,k,l ranges collected	$-17 \le h \le 28$	$-20 \le h \le 20$	$-17 \le h \le 9$	$-18 \le h \le 19$

	$-15 \leq k \leq 15$ $-26 \leq l \leq 26$	$-32 \leq k \leq 33$ $-31 \leq l \leq 31$	$-46 \leq k \leq 43$ $-16 \leq l \leq 18$	$-22 \leq k \leq 21$ $-27 \leq l \leq 26$
θ range for data collection (deg)	1.69 to 25.10	1.274 to 30.127	1.038 to 25.162	1.291 to 27.570
number of reflns collected	87841	88521	58726	84086
number of unique reflns	6187	22020	27140	22911
number of parameters	407	902	1984	1198
data to parameter ratio	6187/407	22020/902	27140/1984	22911/1198
refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
R_1[a]	0.0462	0.0391	0.0479	0.0370
wR_2[b]	0.1242	0.1017	0.1235	0.1010
Goodness-of-fit on F^2[c]	1.0335	1.0610	0.9776	1.0138
largest diff peak and hole ($e/Å^3$)	-0.89 and 0.69	-0.65 and 0.89	-0.57 and 0.65	-0.62 and 0.65

[a] $R_1 = (||F_o| - |F_c||) / |F_o|$. [b] $wR_2 = [[w(F_o^2 - F_c^2)^2] / [w(F_o^2)^2]]^{1/2}$. [c] Goodness-of-fit = $[[w(F_o^2 - F_c^2)^2]/(N_{observns} - N_{params})]^{1/2}$, all data

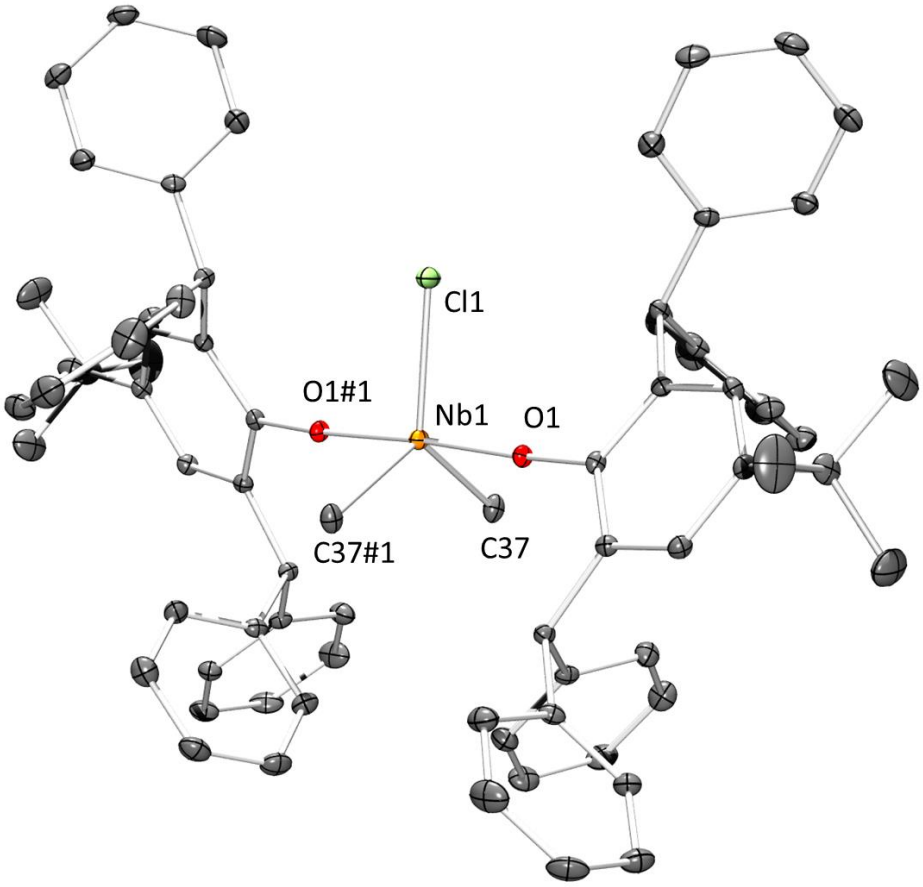

Figure S16. The molecular structure of $[(Ar'O)_2Nb(CH_3)_2(Cl)]$ (**1**) with thermal ellipsoids at the 50% probability level. Hydrogen atoms have been excluded for clarity. Selected bond lengths (Å) and angles (deg): Nb1-O1, 1.895(2); Nb1-Cl1, 2.3578(13); Nb1-C37, 2.135(4); O1#1-Nb1-O1, 176.41(14); Cl1-Nb1-C37, 120.53(11); C37#1-Nb1-C37, 118.9(2); O1-Nb1-C37, 87.94(12); O1-Nb1-C37#1, 90.24(12); Cl1-Nb1-O1, 91.80(7).

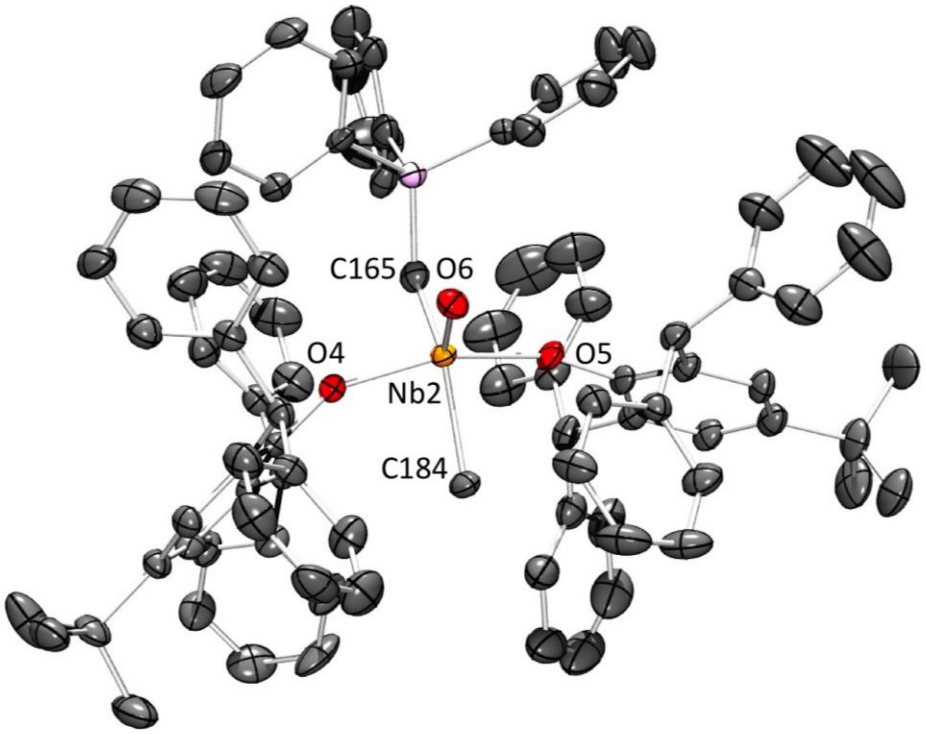

Figure S17. The molecular structure of $[(Ar'O)_2Nb{=}O(CH_3)(H_2CPPh_3)]$ (**3**) with thermal ellipsoids at the 50% probability level. Hydrogen atoms have been excluded for clarity. Selected bond lengths (Å) and angles (deg): Nb1-O1, 1.935(3); Nb1-O2, 1.959(3); Nb1-O3, 1.713(3); Nb1-C73, 2.2.331(4); Nb1-C92, 2.230(4); O1-Nb1-O2, 155.03(12); O1-Nb1-O3, 103.00(13); O2-Nb1-O3, 101.28(13); O1-Nb1-C73, 86.58(14); O2-Nb1-C73, 89.24(14); O3-Nb1-C73, 113.10(15); O1-Nb1-C92, 83.61(14); O2-Nb1-C92, 83.06(14); O3-Nb1-C92, 109.07(15); C73-Nb1-C92, 137.82(15). Two molecules of **3** comprise the asymmetric unit but only one is shown for clarity.

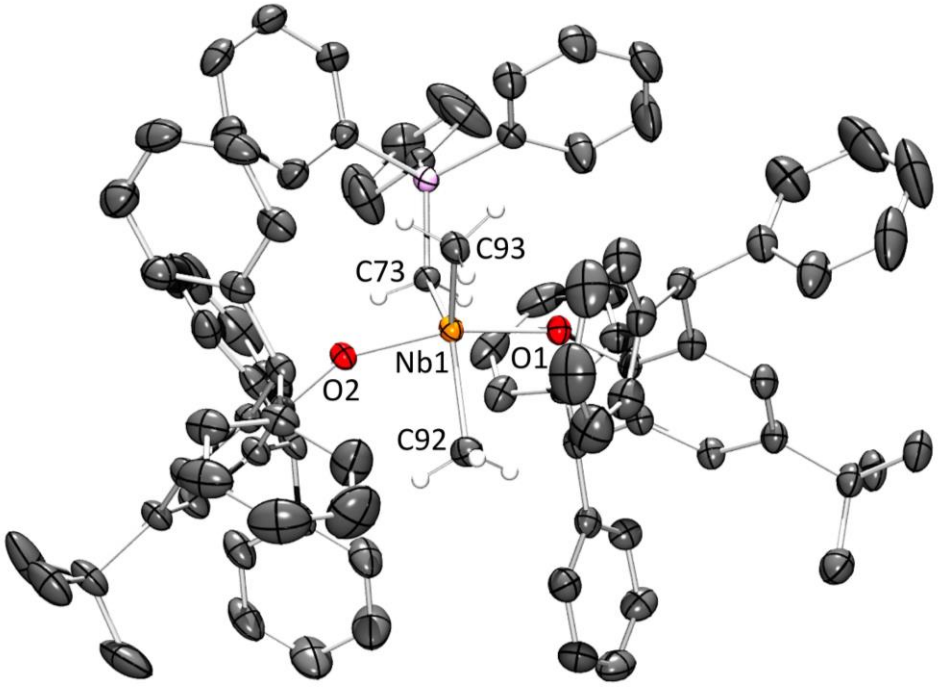

Figure S18. The molecular structure of $[(Ar'O)_2Nb(CH_3)_2(H_2CPPh_3)][CPh(SO_2CF_3)_2]$ (**4**) with thermal ellipsoids at the 50% probability level. Only α-hydrogens of **4** are shown for clarity. Selected bond lengths (Å) and angles (deg): Nb1-O1, 1.8829(12); Nb1-O2, 1.9055(11); Nb1-C73, 2.2226(17); Nb1-C92, 2.1579(18); Nb1-C93, 2.1222(18); O1-Nb1-O2, 165.04(5); O1-Nb1-C73, 91.64(6); O2-Nb1-C73, 91.02(6); O1-Nb1-C92, 84.98(6); O2-Nb1-C92, 81.85(6); C73-Nb1-C92, 128.46(7); O1-Nb1-C93, 96.64(6); O2-Nb1-C93, 95.43(6); C73-Nb1-C93, 115.90(7); C92-Nb1-C93, 115.57(7). The $CPh(OTf)_2$ anion was omitted for clarity.

Computational Details

All calculations were carried out using Density Functional Theory as implemented in the Jaguar 7.7 suite of ab initio quantum chemistry programs.[10] Geometry optimizations were performed with the B3LYP[11-13] functional using the Los Alamos LACVP**[14-16] basis set, which includes relativistic effective core potentials. Vibrational frequency calculations based on analytical second derivatives at the B3LYP/6-31G** level of theory were carried out to confirm that all structures are proper minima.

Calculations were initially performed on a model complex (**2m**), in which the phenyl and t-butyl substituents on the aryloxides were replaced with methyl groups, resulting in a complex of 110 atoms: $[(ArO)_2Nb{=}CH_2(CH_3)(H_2CPPh_3)]$ (Ar = (2,6-iPr_2)-4-Me-C_6H_2) (**2m**). Complexes **2** and **2m** showed a similar orbital picture; with a comparable HOMO-LUMO gap (3.736 and 3.418 eV, Table S2). Cartesian coordinates and vibrational frequencies of both complexes are provided in Table S3 and S4.

Table S2. Energies of Calculates Complexes

	2	**2m**
Total energy (kcal·mol^{-1})	-2601105.41	-1490562.02
Total energy (eV)	-112794.840	-64637.021
Entropy (kcal·mol^{-1}), T=298.15 K	964.76	591.11
ZPE (cal·mol^{-1}), T=0 K	471.64	327.38
HOMO (eV)	-4.789	-4.700
LUMO (eV)	-1.152	-1.282

Table S3. Cartesian Coordinates in Å of Calculated Complexes

==========

$[(Ar'O)_2Nb{=}CH_2(CH_3)(H_2CPPh_3)]$ (**2**)

==========

C	1.414755991	0.755133039	-7.576902003
C	3.890493667	0.648421445	-7.093317105
C	2.729577536	2.857518329	-7.233218865
C	2.573457320	1.395710427	-6.774434155
C	0.131915255	-4.254111831	-5.773972127
C	1.466587605	-4.344993205	-5.384552150
C	-0.692140853	-3.299004994	-5.174114082
C	2.266444581	1.286164191	-5.269547170
C	2.147132793	0.025726217	-4.669326743
C	1.975520868	-3.492656336	-4.401921382
C	2.070056913	2.390745629	-4.442670483
C	-0.048571311	6.380122454	-4.191218266
C	-0.181036966	-2.449685944	-4.194824864
C	-1.390589855	6.140370792	-3.901993933
C	1.158448558	-2.537445250	-3.787679232
C	0.945646255	5.565545336	-3.646598211
C	-1.732718006	5.084668011	-3.055224653
C	1.843987552	-0.147469063	-3.320039003
C	1.800805614	2.277883551	-3.072434769
C	0.611767506	4.494181525	-2.810530952
C	1.680763338	-1.551283733	-2.737357180
C	-0.739612183	4.269327873	-2.516073447
C	4.165023410	4.069641226	-2.658133660
C	1.665025996	0.994291327	-2.499490255
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C	-5.470240686	3.171526074	-1.826826945
C	-1.431178603	-5.536618192	-1.934673996
C	1.662164430	3.540951557	-2.227677033
C	2.925999775	-2.081687606	-2.023400923

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O	1.367350959	0.851810453	-1.183476054
O	-1.536886222	-0.283743108	1.112246806
P	2.383517363	-0.152200825	2.890392716
Nb	-0.026492086	0.575975993	0.193414149

==========

[$(ArO)_2Nb{=}CH_2(CH_3)(H_2CPPh_3)$]

(Ar = (2,6-iPr_2)-4-Me-C_6H_2) (**2m**)

==========

C	3.689206110	1.334511886	-6.275847941
C	3.001489697	1.240411971	-4.932098025
C	2.784068453	-0.000441821	-4.323369145
C	2.555194153	2.378346486	-4.259030406
C	1.332115425	-2.514537035	-3.425831607
C	2.165812409	-0.126504456	-3.078145788
C	1.919685698	2.318216217	-3.013333116
C	0.466428478	4.388998951	-3.241260317
C	1.965824568	-1.502006379	-2.452795510
C	1.740525555	1.050650340	-2.412863340
C	1.430569188	3.595227835	-2.338351314
C	3.288474050	-2.047931435	-1.873161425
C	2.604185372	4.481232256	-1.873052086
C	-1.613571752	0.828263856	-1.645606289
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H	-6.185717643	-0.428089215	1.496924731
H	-3.118051157	1.645205898	1.085451467
H	0.286268212	3.289553752	0.715821224
H	1.976495078	-1.210371554	0.734860832
H	6.986864524	2.507905371	0.744541283
H	0.615795086	-1.417066609	1.862987660
H	-1.053996561	2.655505900	1.795961595
H	3.431271436	-2.683887104	2.183573923
H	4.356863807	-4.497061857	3.583247814
H	6.950712871	1.616559414	3.067451668
H	-0.315312226	-0.308290023	3.991673835
H	4.938529689	0.485519356	3.931985297
H	2.894331971	2.568464280	3.967536775
H	-1.542485628	1.080206046	5.614132824
H	4.395382329	-4.266050604	6.059294452
H	1.644671962	3.964999571	5.575824179
H	2.591256324	-0.380862288	5.731392574
H	-0.574430331	3.225717283	6.413940209
H	3.506137404	-2.204066714	7.125327981
O	1.193557377	0.970985050	-1.174200050
O	-1.685568841	-0.288604627	0.999141841
P	2.303516389	-0.075610769	2.752716438
Nb	-0.247285035	0.707422202	0.129947379
H	-0.964057604	-3.163073834	2.489321849
H	-1.820902291	-4.616402835	1.963548293
H	-0.146943343	-4.344824007	1.446621229
H	-0.799565631	-4.516656039	-1.045645070
H	-2.449597163	-4.908142669	-0.563161052
H	-2.155058938	-3.563206875	-1.677054659
H	-5.062446672	3.094053783	1.039303365
H	-5.304824275	1.801712322	-0.148340892
H	-6.166743039	1.766270641	1.399367201
H	-3.052736627	1.041139982	3.487561362
H	-3.874652550	2.594641598	3.261824181
H	-4.820278441	1.127810959	3.579443215
H	0.063492207	5.254667732	-2.701972070
H	0.965113561	4.763904976	-4.142894787
H	-0.376722647	3.766981222	-3.558620780
H	2.233413096	5.389822419	-1.382647994
H	3.244176652	3.953738756	-1.157065017
H	3.231342279	4.790459983	-2.718217944
H	1.101789068	-3.451196450	-2.904925840
H	0.400313602	-2.124721268	-3.849940808
H	2.001539739	-2.761948126	-4.257704506
H	3.723277313	-1.351233552	-1.147076031
H	3.131924044	-3.013535015	-1.375366874
H	4.030599941	-2.199195499	-2.666542866
H	-7.511058569	-2.363002488	1.010060292
H	-6.698990892	-3.869912636	0.270632517
H	-6.734072490	-3.641793532	2.114849665
H	3.739830728	2.369929953	-6.626611393
H	4.716029694	0.949161058	-6.232952429
H	3.161387503	0.750776682	-7.040347616

Table S3. Vibrational Frequencies in cm^{-1} of Calculated Complexes

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$[(Ar'O)_2Nb{=}CH_2(CH_3)(H_2CPPh_3)]$ (**2**)

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2.11 6.91 11.31 14.43 16.71 18.18
19.54 22.47 23.80 25.64 29.18 32.51
35.68 36.87 38.50 39.25 40.26 41.50
42.46 44.16 44.95 46.36 48.27 49.75
50.54 51.35 52.44 54.25 55.12 56.28
58.29 59.82 60.72 62.28 64.67 66.30
67.19 68.48 70.80 73.07 75.40 77.74
82.16 93.19 107.71 109.45 123.09 140.02
143.61 145.43 147.28 150.21 152.22 164.90
180.97 187.19 188.67 201.64 208.94 210.44
217.94 226.76 228.36 230.31 230.83 232.06
234.12 236.19 236.67 237.79 239.09 245.19
246.73 248.60 251.39 256.86 257.96 258.78
267.52 269.39 269.65 281.10 284.85 291.27
293.59 295.28 298.78 300.65 306.25 312.13
315.26 319.37 325.79 332.52 333.22 351.47
352.17 373.52 376.87 377.53 402.19 404.91
405.24 408.51 412.03 414.23 414.82 415.07
415.82 417.83 418.85 419.25 419.74 421.56
426.76 437.00 448.92 451.38 456.25 466.55
473.04 479.46 481.20 487.58 488.12 490.02
502.37 505.94 506.68 510.16 511.16 512.46
514.81 534.60 535.45 537.28 551.61 555.91
571.88 580.36 582.00 599.79 601.10 613.40
619.35 619.95 626.54 627.97 629.47 629.90
631.41 632.39 632.74 633.07 633.59 634.19
635.66 646.37 646.65 652.90 654.91 658.51
659.35 671.17 675.07 687.56 694.25 696.68
697.41 701.48 706.18 709.69 710.21 717.10
717.92 718.35 718.69 719.40 719.83 720.82
721.28 721.60 728.00 750.18 756.67 757.10
760.22 761.46 764.14 767.43 771.96 772.02
772.97 774.42 777.68 781.74 782.97 810.89
821.00 822.43 843.44 844.01 846.39 847.09
864.67 864.93 865.41 866.49 867.40 868.14
868.52 869.18 869.53 869.85 870.84 871.58
872.25 877.00 878.52 883.16 891.28 916.68
919.52 929.99 931.58 933.51 933.82 934.97
935.81 937.46 939.51 939.81 941.83 942.56
942.88 943.99 944.12 944.45 946.06 956.66
964.79 966.02 966.32 966.88 967.33 976.02
976.49 977.92 978.21 980.55 981.53 981.63
984.91 985.13 986.27 992.33 992.97 993.75
995.19 997.80 998.52 999.36 999.62 1000.05
1001.95 1002.18 1007.87 1009.31 1009.53 1011.42
1012.02 1014.74 1015.06 1015.60 1016.52 1016.81
1017.05 1017.34 1017.97 1022.38 1042.28 1050.83
1051.94 1052.39 1054.01 1054.44 1054.92 1056.45
1057.29 1058.20 1058.53 1059.24 1059.43 1059.67
1059.99 1060.16 1109.63 1110.28 1110.80 1110.88
1110.94 1111.43 1112.45 1112.59 1112.93 1114.23
1114.63 1117.68 1126.66 1130.60 1146.72 1149.80
1186.16 1186.58 1187.05 1187.20 1187.55 1187.72
1188.08 1188.24 1190.67 1191.53 1192.83 1194.04
1194.17 1195.03 1195.45 1202.65 1205.18 1206.15
1207.14 1209.41 1211.03 1211.50 1212.15 1212.46
1213.48 1214.45 1215.35 1216.18 1216.45 1218.25
1219.98 1221.62 1223.87 1231.28 1231.56 1235.38
1236.01 1261.33 1266.00 1271.69 1274.14 1279.50
1284.22 1285.55 1286.95 1294.10 1296.33 1303.59
1314.16 1317.07 1318.00 1329.01 1333.08 1333.49
1335.14 1336.69 1337.36 1351.26 1355.73 1364.41
1364.63 1364.79 1365.00 1365.55 1365.70 1366.32
1366.74 1367.71 1368.09 1368.71 1369.25 1369.64
1371.06 1372.11 1376.08 1377.25 1410.39 1410.87
1412.04 1412.28 1422.34 1443.05 1443.70 1458.56
1462.02 1462.72 1475.70 1476.66 1477.49 1478.95
1485.30 1486.77 1488.28 1489.71 1491.26 1492.32
1493.86 1495.34 1495.37 1495.72 1495.79 1496.75
1499.75 1500.05 1505.06 1505.22 1517.90 1518.30
1520.49 1520.73 1527.22 1530.20 1530.38 1533.64
1533.75 1535.66 1536.99 1537.54 1538.06 1538.82
1539.03 1539.44 1540.04 1610.41 1612.63 1627.16
1629.52 1631.14 1635.49 1636.60 1637.42 1637.91
1641.01 1641.79 1643.57 1643.63 1644.05 1646.01
1646.60 1653.89 1655.07 1657.26 1657.89 1658.39
1659.64 1662.14 1662.43 1662.61 1664.55 3010.81
3033.40 3034.14 3035.59 3037.03 3043.15 3043.83
3051.33 3052.67 3067.64 3086.92 3098.93 3100.65
3101.53 3103.21 3105.68 3106.15 3110.42 3110.98
3112.99 3114.34 3115.35 3118.27 3122.28 3122.67
3126.19 3135.13 3144.69 3166.76 3168.02 3168.58
3169.03 3170.07 3172.82 3173.57 3174.07 3176.88
3177.10 3177.37 3178.14 3178.30 3178.50 3180.65
3181.68 3183.63 3184.48 3185.70 3186.08 3186.42
3186.96 3187.23 3187.53 3191.61 3191.81 3192.63
3193.19 3194.65 3195.75 3196.06 3196.62 3197.07
3197.93 3199.53 3200.31 3200.89 3201.02 3201.55
3203.47 3203.84 3203.89 3205.15 3206.42 3207.18
3207.67 3208.02 3208.94 3209.44 3210.43 3211.34
3212.13 3212.36 3214.10 3214.82 3215.47 3219.68
3223.95 3224.18 3232.68

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$[(ArO)_2Nb{=}CH_2(CH_3)(H_2CPPh_3)]$
(Ar = (2,6-iPr_2)-4-Me-C_6H_2) (**2m**)

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10.21 13.29 17.51 22.16 24.31 25.57
29.25 35.00 38.98 40.25 41.91 48.51
48.84 51.34 56.36 57.69 58.76 61.15
64.14 66.57 70.95 75.99 78.86 89.02
97.38 109.12 128.94 135.41 137.09 138.20
140.50 145.25 162.19 179.65 185.56 189.44
191.62 202.71 213.92 214.56 219.21 238.72
244.10 244.94 245.53 248.67 249.78 250.68
253.27 256.79 261.89 264.08 268.26 270.08
272.80 273.39 285.95 297.39 304.70 308.84
322.11 327.37 331.15 332.40 357.02 367.83
386.57 402.35 404.82 409.82 413.36 427.53
432.45 434.62 436.49 439.95 447.52 453.88
464.83 469.33 472.72 490.60 503.17 509.43
534.52 542.68 547.72 556.28 561.82 574.67
586.79 596.37 603.03 606.32 611.72 627.87
628.84 630.24 630.51 630.88 633.71 636.14
637.69 656.15 686.62 694.48 704.92 710.02
710.27 717.88 726.53 749.78 763.01 766.79
770.60 782.16 784.84 810.20 820.57 824.61
861.48 866.89 869.52 872.76 880.61 882.37
884.87 890.04 890.80 909.69 913.92 919.97
932.71 935.58 936.52 937.37 938.71 944.36
954.48 957.86 960.06 962.34 964.98 966.03
966.56 968.57 969.65 983.24 984.55 999.36
1008.03 1010.25 1012.05 1013.12 1015.08 1025.18
1025.88 1031.36 1052.12 1054.39 1056.70 1064.08
1092.86 1100.94 1111.62 1111.89 1113.49 1113.61
1114.71 1116.49 1122.10 1123.99 1126.54 1127.24
1129.62 1132.61 1140.34 1145.70 1149.64 1164.51

1192.51	1192.66	1193.13	1198.75	1200.06	1201.60
1203.76	1206.73	1217.48	1219.96	1225.08	1248.70
1260.18	1281.11	1282.51	1294.71	1303.54	1315.14
1322.84	1328.42	1334.98	1336.60	1337.77	1348.16
1349.74	1360.63	1364.37	1364.77	1367.93	1368.53
1374.66	1374.93	1383.51	1389.02	1406.75	1408.10
1409.56	1410.29	1420.89	1425.35	1428.51	1429.24
1430.76	1431.60	1455.54	1462.39	1463.75	1471.13
1477.33	1477.66	1479.84	1485.11	1490.22	1493.10
1496.87	1498.27	1498.67	1500.15	1501.27	1503.46
1504.59	1505.07	1506.13	1512.20	1513.34	1515.82
1516.40	1517.79	1520.81	1521.55	1522.08	1523.63
1526.05	1530.28	1531.22	1532.24	1538.86	1619.37

1622.99	1628.29	1631.10	1634.42	1645.70	1646.47
1649.66	1658.35	1658.69	2590.25	2630.35	2695.21
2987.91	3023.36	3027.61	3028.42	3028.53	3030.80
3034.19	3035.74	3036.35	3038.72	3059.71	3070.03
3074.62	3079.25	3079.78	3086.13	3090.24	3091.33
3093.33	3094.44	3094.89	3098.23	3100.01	3101.09
3104.85	3105.26	3107.16	3110.43	3113.05	3114.38
3114.53	3115.27	3115.66	3118.22	3120.59	3127.78
3143.87	3163.65	3165.67	3168.88	3177.45	3180.47
3183.74	3186.72	3188.10	3189.76	3192.73	3195.23
3198.47	3202.65	3203.86	3205.81	3208.66	3212.07
3214.45	3217.89	3218.86			

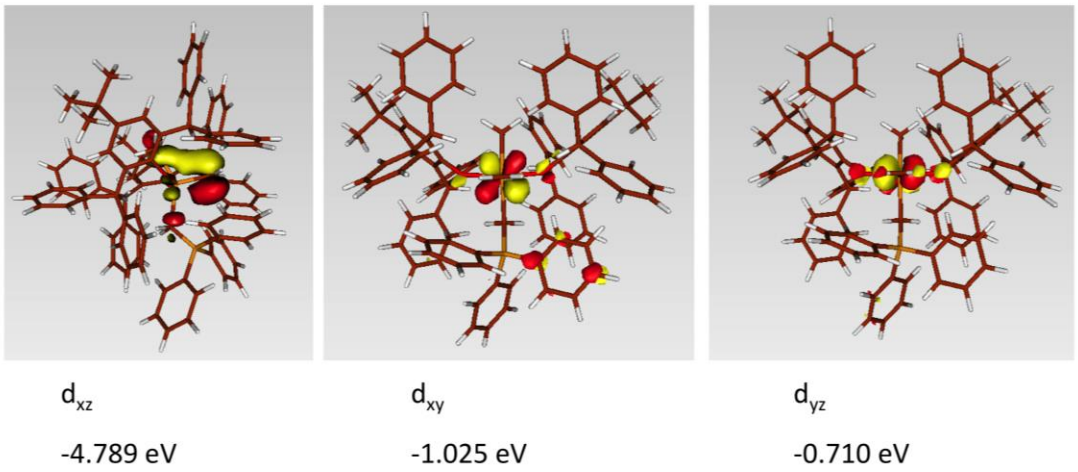

Figure S19. Relevant d-orbitals of 2. (Left) HOMO, (Middle and Right) lowest unoccupied metal-based orbitals.

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