Supporting Information

Visible-Light Driven H_2 Reductive Elimination Unlocks Reactivity in Polyhydrido Niobium Iridium Clusters

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General Considerations

Unless otherwise noted, all reactions were performed either using standard Schlenk-line techniques or in an MBRAUN glovebox under an atmosphere of purified argon (<1 ppm of O_2/H_2O). Glassware and cannulas were stored in an oven at ~100 °C for at least 16 h prior to use. THF and *n*-pentane were purified by passage through a column of activated alumina, dried over Na/benzophenone, vacuum-transferred to a storage flask, and freeze–pump–thaw degassed prior to use. Deuterated solvents (toluene-d_8, THF-d_8, and C_6D_6) were dried over Na/benzophenone, vacuum-transferred to a storage flask, and freeze–pump–thaw degassed prior to use. High purity CO_2 (99.999%) was purchased from Air Liquide. The synthesis of Cp*IrH_4 was carried out following a literature procedure.[1] Pentakis(dimethylamido)niobium(V), $Nb(NMe_2)_5$, was purchased from Strem Chemicals (#41-5300) and used as received. All other reagents were acquired from commercial sources and used as received.

IR Spectroscopy

The samples were prepared in a glovebox (diluted in dry KBr powder), sealed under argon in a Diffuse Reflectance Infrared Fourier Transform (DRIFT) cell fitted with KBr windows, and then analyzed using a Nicolet 670 FT-IR spectrometer.

Elemental Analyses

Elemental analyses were performed under an inert atmosphere at Mikroanalytisches Labor Pascher, Germany.

X-Ray Diffraction - Structural Determinations

Suitable crystals were coated in parabar oil, selected manually under a binocular microscope and mounted on a Rigaku-OD Synergy-S single-crystal diffractometer equipped with an Hypix-100 detector. Intensities were collected at 100K with molybdenum radiation (λ=0.71073 Å) or copper radiation (λ=1.54184 Å) for compounds **1-6** and (Cp*IrH_3)(Cp*IrH_2)$Nb(NMe_2)_2$ by means of the CrysalisPro software.[2] Reflection indexing, unit-cell parameters refinement, Lorentz-polarization correction, peak integration and background determination were carried out with the CrysalisPro software.[2] An analytical absorption correction was applied using the modeled faces of the crystal.[3] The resulting set of *hkl* was used for structure solution and refinement. The structures were solved with the ShelXT structure solution program using the intrinsic phasing solution method and by using Olex2 as the graphical interface.[4,5] The model was refined with version 2018/3 of ShelXL using least-squares minimization.[4] CCDC 2487215-2487221 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Date Centre via www.ccdc.cam.ac.uk/data_request/cif.

NMR Spectroscopy

Solution NMR spectra were recorded on Bruker AV-300 and AV-500 spectrometers. ^1H and ^{13}C chemical shifts were measured relative to residual solvent peaks, which were assigned relative to an external TMS standard set at 0.00 ppm. ^1H and ^{13}C NMR assignments were confirmed by ^1H–^1H COSY, ^1H–^{13}C HSQC, and HMBC experiments. NMR data recorded as follows: chemical shift (δ) [multiplicity, coupling constant(s) *J* (Hz), relative integral], where multiplicity is defined: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or combinations thereof, and prefixed br = broad.

UV-Visible Spectroscopy

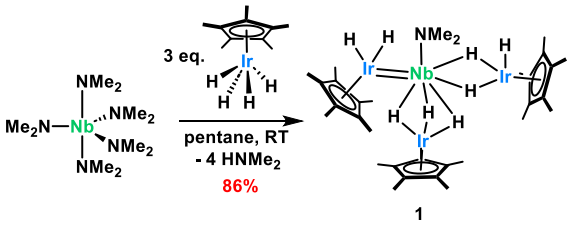
Samples were dissolved in *n*-pentane and transferred to a quartz cuvette equipped with a J. Young valve inside an argon-filled glove box. Solvent backgrounds were subtracted manually from an appropriate solvent blank experiment. Absorption spectra were recorded on a Perkin-Elmer Lambda 1050 UV/Vis/NIR spectrophotometer.

UV Light Source and Photolysis Experimental Set-up

The light source used in this work is an Asahi MAX-303 300W Xenon light source which delivers broad spectrum light in a range of 250 nm - 1000 nm with a RLQL80 collimator lens. The light source can be equipped with a 400 nm long pass filter if needed. In a typical photolysis experiment, the sample to be irradiated was placed between 5-10 cm away from the collimator lens.

Syntheses

Synthesis of complex **1**



In an argon-filled glovebox, a 50 mL Schlenk flask was charged with 0.050 g of $Nb(NMe)_5$ ($1.59e^{-5}$ mol, 1 eq) and dissolved in 25 mL pentane. To this solution was added in one portion 0.161 g Cp^*IrH_4 ($4.87e^{-5}$ mol, 3.05 eq) and the solution was stirred overnight. The volatile materials were removed under reduced pressure and the orange solid was then recrystallized from a saturated solution of pentane cooled to -40°C to yield large red block shaped crystals of analytically pure **1**. Mass = 0.154 g, Yield = 86%

^{1}H NMR (500 MHz, C_6D_6, 298 K) δ 3.31 (6H, s, N**Me**$_2$), 2.16 (45H, s, Cp*); -13.50 (8H, s, Ir – **H)**

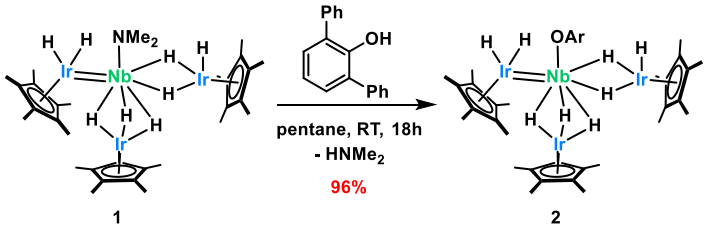
^{13}C NMR (126 MHz, C_6D_6, 298 K) δ 92.5 (Cp*), 50.1 (Nb – N**Me**$_2$), 11.00 (Cp*-**Me**)

DRIFT: ν3025 – 2724 (ν C-H), 2256 – 1831 (ν M-H) cm^{-1}

UV-Vis, pentane, nm (ε x10^3, $M^{-1}cm^{-1}$): 205 (78), 239 (57), 315 (32), 395 (10)

EA: Calculated for $C_{32}H_{59}NNbIr_3$: C 34.09, H 5.28, N 1.24. Found C 33.95, H 5.27, N 1.07

Synthesis of complex **2**



In an argon-filled glovebox with the lights shut off and room lights dimmed as low as possible, a 20 mL scintillation vial was charged with 20 mg of complex **1** ($1.77e^{-5}$ mol, 1 eq) and dissolved in 5 mL pentane. To this solution was added 4.3 mg 2,6-diphenylphenol ($1.77e^{-5}$ mol, 1 eq) in one portion and the vial was tightly wrapped in aluminum foil to exclude light. This solution was stirred for 18h at room temperature before the volatile materials were removed under reduced pressure to yield 22.6 mg of analytically pure **2**. Yield = 96%

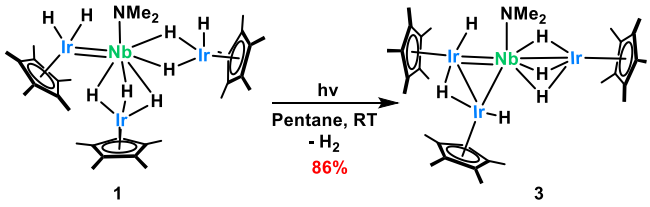
^{1}H NMR (500 MHz, C_6D_6, 298 K) δ 7.86 (dd, *J* = 8.1, 1.1 Hz, 4H, **H**-C_{aryl}), 7.34 (t, *J* = 7.7 Hz, 4H, **H**-C_{aryl}), 7.24 (d, *J* = 7.5 Hz, 2H, **H**-C_{aryl}), 7.19 (t, *J* = 7.4 Hz, 2H, **H**-C_{aryl}), 6.90 (t, *J* = 7.5 Hz, 1H, **H**-C_{aryl}), 1.98 (s, 45H, C-**H**$_{Cp*}$), -13.36 (s, 8H (Ir - **H**).

^{13}C NMR (126 MHz, C_6D_6, 298 K) δ 160.62 (**C**O-Nb), 141.73 (**C**$_{Ar}$), 132.87 (**C**$_{Ar}$), 130.88 (**C**$_{Ar}$), 130.83 (**C**$_{Ar}$), 130.11 (**C**$_{Ar}$), 125.73 (**C**$_{Ar}$), 119.90 (**C**$_{Ar}$), 93.01 (**Cp***), 10.82 (Cp*-**Me**).

DRIFT: 3025 – 2903 (ν C-H), 2244 – 1789 (ν M-H) cm^{-1}

EA: Calculated for $C_{48}H_{66}ONbIr_3$: C 43.39, H 5.01. Found: C 43.57, H 4.80

Synthesis of complex **3**



In an argon-filled glovebox, a Teflon capped 100 mL Schlenk flask was charged with 0.050 g of complex **1** and dissolved in 25 mL pentane. This solution was brought out of the glovebox and exposed to the 300 W light source overnight, yielding a dark brown solution. The volatile materials were removed under reduced pressure and the solid recrystallized from a saturated pentane solution at -40°C. While by ^{1}H NMR the conversion is quantitative, after recrystallization only 0.043 g could be recovered giving a recovered yield of 86%.

^{1}H NMR (500 MHz, C_6D_6, 298 K) δ 3.40 (s, 6H, N**Me**$_2$), 2.32 (s, 30H, Cp*), 1.98 (s, 15H, Cp*), -13.03 (s, 6H, Ir – **H**).

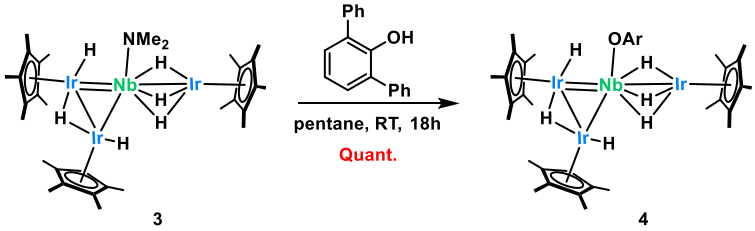
^{13}C NMR (126 MHz, C_6D_6, 298 K) δ 93.11 (**Cp***Ir=Nb), 91.06 (**Cp***Ir-Nb), 46.28 (N**Me**$_2$), 12.00 (**Me**-Cp*Ir=Nb), 10.89 (**Me**-Cp*Ir-Nb)

DRIFT: 3040 – 2697 (ν C-H), 2213 – 1831 (ν M-H) cm^{-1}

UV-Vis, pentane, nm (ε x10^3, M^{-1}cm^{-1}): 205 (68), 250 (47), 293(28), 367 (13)

EA: Calculated for $C_{32}H_{57}NNbIr_3$: C 34.15, H 5.11, N 1.24. Found C 34.12, H 4.78, N 1.23

Synthesis of complex **4**



In an argon-filled glovebox, a 20 mL scintillation vial was charged with 0.025 g of complex **3** (2.2e^{-5} mol, 1 eq) and dissolved in 10 mL pentane. To this rapidly stirring solution was added 4.3 mg diphenylphenol (2.2e^{-5} mol, 1 eq) in one portion. The solution was left to stir overnight at room temperature before the volatile materials were removed under reduced pressure to yield 0.027 g analytically pure **4** in quantitative yield.

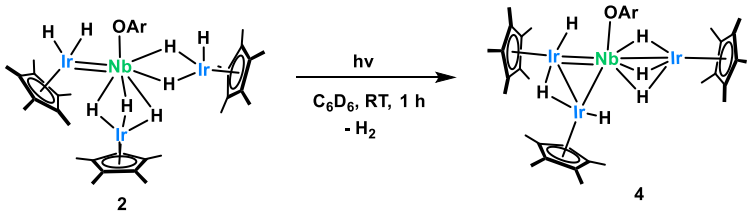
^{1}H NMR (500 MHz, C_6D_6, 298 K) δ 7.92 – 7.84 (d, *J* = 7.6 Hz, 4H, **H**-C_{Arl}), 7.35 – 7.25 (m, 6H, **H**-C_{Arl}), 7.19 (d, *J* = 7.3 Hz, 2H, **H**-C_{Arl}), 6.94 (t, *J* = 7.5 Hz, 1H, **H**-C_{Arl}), 2.08 (s, 30H, Cp*), 1.92 (s, 15H, Cp*), -14.38 (s, 6H, Ir – **H**).

^{13}C NMR (126 MHz, C_6D_6, 298 K) δ 160.43 (**C**O–Nb), 141.82 (**C**$_{Ar}$), 132.20 (**C**$_{Ar}$), 130.87 (**C**$_{Ar}$), 130.11 (**C**$_{Ar}$), 127.82 (**C**$_{Ar}$), 125.70 (**C**$_{Ar}$), 119.15 (**C**$_{Ar}$), 92.58 (**Cp***-Me), 91.50 (**Cp***-Me), 11.46(Cp*-**Me**), 10.65(Cp*-**Me**).

DRIFT: 3129 – 2773 (ν C-H), 2197 – 1798 (ν M-H) cm^{-1}

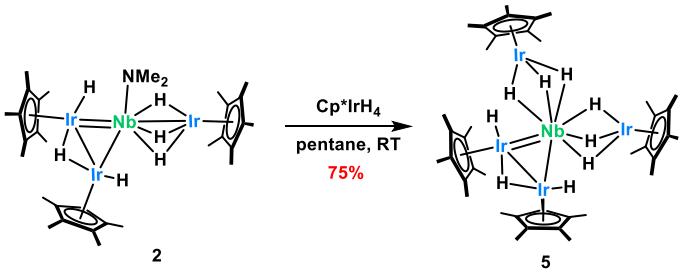
EA: Calculated for $C_{48}H_{64}ONbIr_3$: C 43.46, H 4.86. Found: C 43.71, H 4.70

Synthesis of complex **4** from the photolysis of **2**



A Teflon capped J-Young NMR tube was charged with 0.0082 g of complex **2** and dissolved in 0.5 mL C_6D_6. The solution was exposed to the unfiltered light source as described above. Within one hour of irradiation, quantitative conversion to complex **4** had ben observed by ^{1}H NMR spectroscopy. The photolysis of this complex was also observed in the glovebox when a pentane solution of complex **2** was exposed to ambient light. After 24 hours at rt under ambient light, total consumption of complex **2** was observed with the clean conversion to complex **4**.

Synthesis of complex **5**



In an argon-filled glovebox, a 20 mL scintillation vial was charged with 0.025 g of complex **3** ($2.2e^{-5}$ mol, 1 eq.) and dissolved in 10 mL pentane. To this solution was added 7.3 mg Cp^*IrH_4 ($2.2e^{-5}$ mol, 1 eq.) in one portion. The solution was left to react for 18h at room temperature before the volatile materials were removed under reduced pressure. The dark brown solid was recrystallized from a saturated pentane solution cooled to -40°C to yield dark brown rod-shaped crystals suitable for X-ray crystallography. While by ^{1}H NMR the conversion is quantitative, after recrystallization only 0.024 g could be recovered giving a recovered yield of 75%.

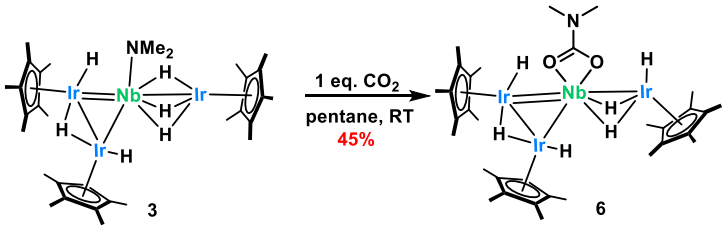
^{1}H NMR (500 MHz, C_6D_6, 298 K) δ 2.30 (s, 30H, Cp*), 2.11 (s, 30H, Cp*), -14.17 (s, 9H, Ir-**H**).

^{13}C NMR (126 MHz, C_6D_6, 298 K) δ 92.54 (**Cp***-Me), 91.87 (**Cp***-Me), 11.65 (Cp*-**Me**), 10.85 (Cp*-**Me**).

DRIFT: 3067 – 2716 (ν C-H), 2237 – 1835 (ν M-H) cm^{-1}

EA: Calculated for $C_{40}H_{69}NbIr_4$: C 34.03, H 4.93. Found: C 34.31, H 4.91

Synthesis of complex **6**



Inside an argon-filled glovebox, a teflon screw-capped double Schlenk flask (volume = 72.1 mL) was charged with 0.050 g of complex **3** ($4.4e^{-5}$ mol, 1 eq) and dissolved in 20 mL pentane. The vessel was taken outside the glovebox, the pentane solution was frozen in a liquid nitrogen bath and the atmosphere was degassed to remove argon. Then, 15.2 mBar high purity CO_2 ($4.4e^{-5}$ mol, 1 eq) was added at room temperature. The solution quickly darkened and the solution was left to react for 3h at room temperature. The volume was reduced to 10 mL under reduced pressure and cooled to -40°C from which dark brown needle crystals could be obtained, suitable for X-ray diffraction. While by NMR the conversion is quantitative, after recrystallization only 0.023 g of material could be recovered giving a recovered yield of 45%.

^{1}H NMR (500 MHz, C_6D_6, 298 K) δ 2.38 (s, 30H, Cp*), 2.36 (s, 6H, N**Me**$_2$), 2.00 (15, 5H, Cp*), -12.66 (s, 6H, Ir – **H**).

^{13}C NMR (126 MHz, C_6D_6, 298 K) δ 163.54 (Me_2N–**C**O_2), 93.41 (**Cp***-Me), 92.10 (**Cp***-Me), 34.06 (N**Me**$_2$), 11.67 (Cp*-**Me**), 10.64 (Cp*-**Me**).

DRIFT: 3106 – 2736 (ν C-H), 2240 – 1897 (ν M-H), 1574 (ν C=O) cm^{-1}

EA: Calculated for $C_{33}H_{57}NO_2NbIr_3$: C 33.90, H 4.91, N 1.20. Found C 34.84, H 4.80, N 1.11

NMR spectra

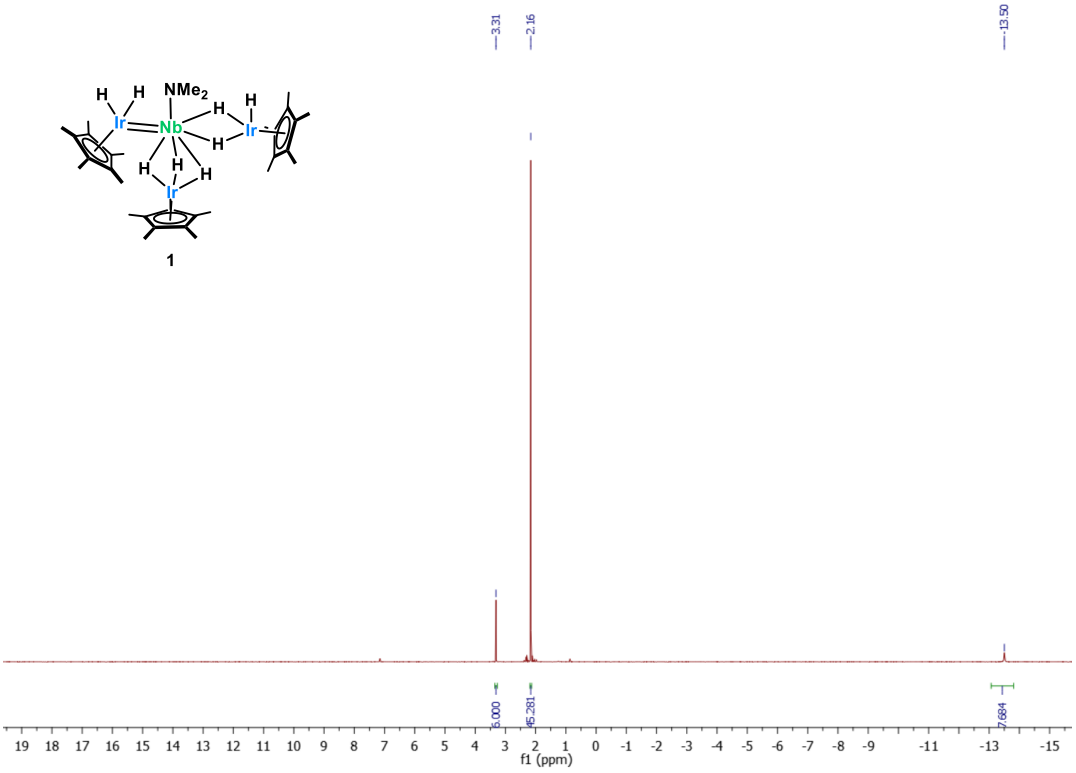


Figure S 1 : ^{1}H NMR spectrum of complex 1 in C_6D_6 (298K, 500 MHz).

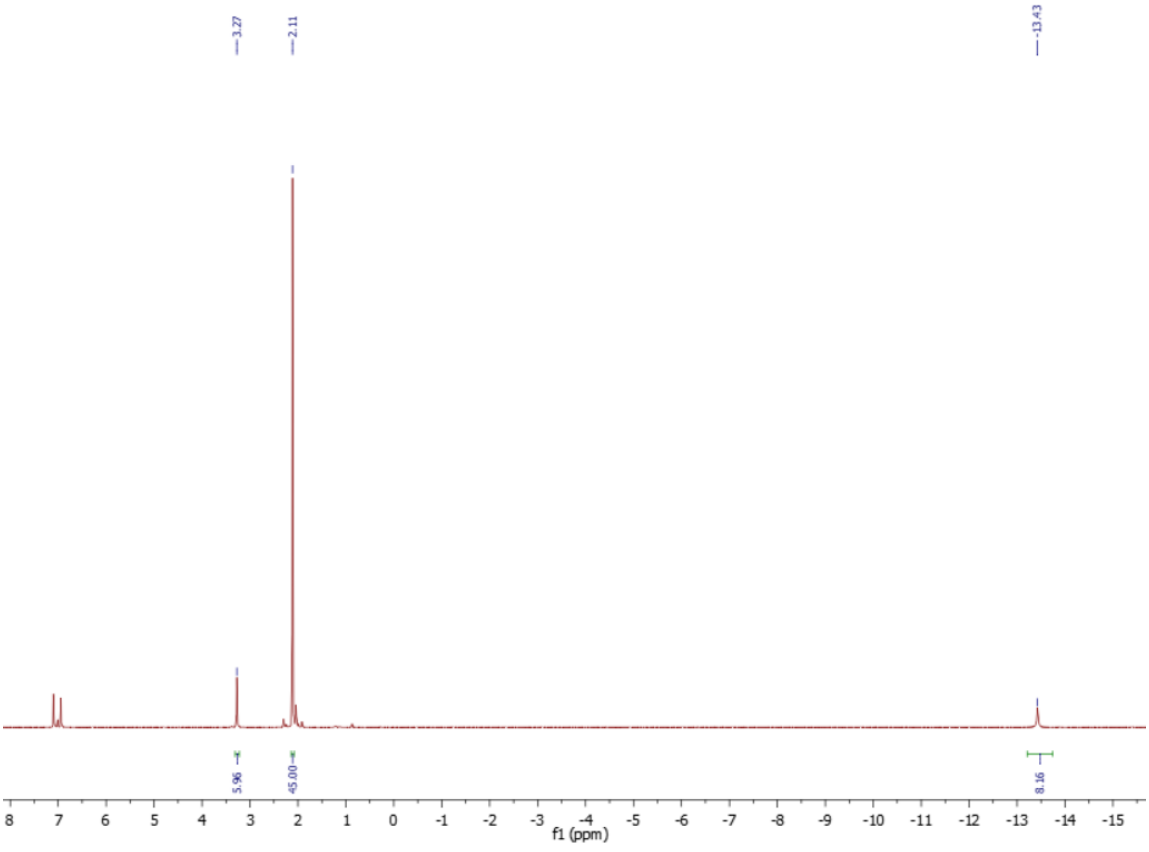


Figure S 2 : ^{1}H NMR spectrum of complex 1 in d_8-toluene recorded at -35 °C (500 MHz).

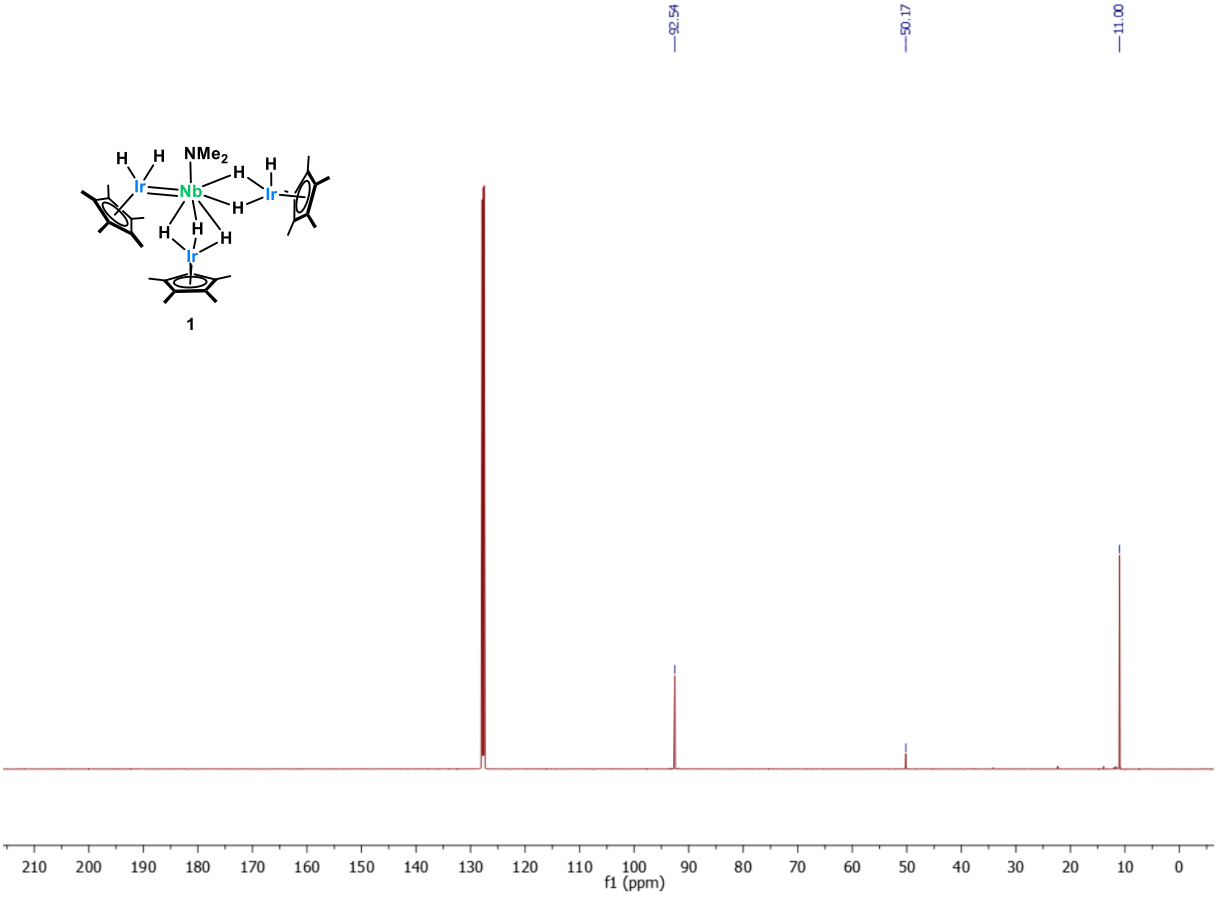


Figure S 3 : ^{13}C NMR spectrum of complex 1 in C_6D_6 (298K, 125 MHz).

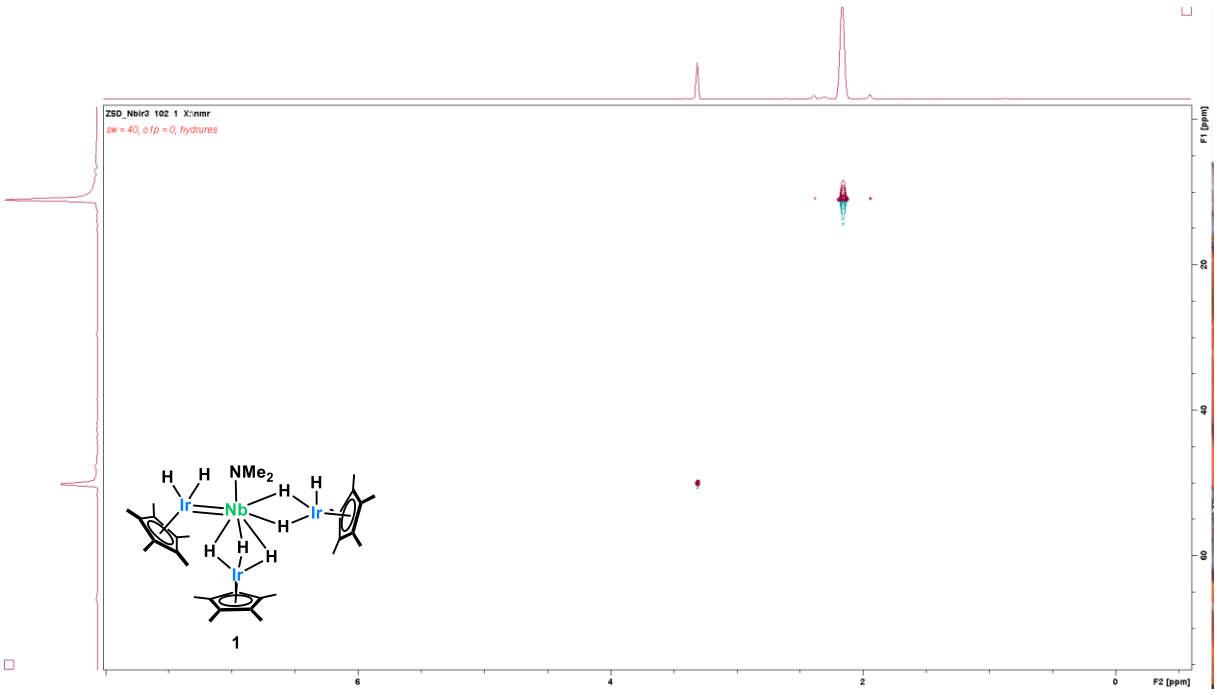


Figure S 4 : ^{1}H ^{13}C HSQC NMR spectrum of complex 1 in C_6D_6 (298K).

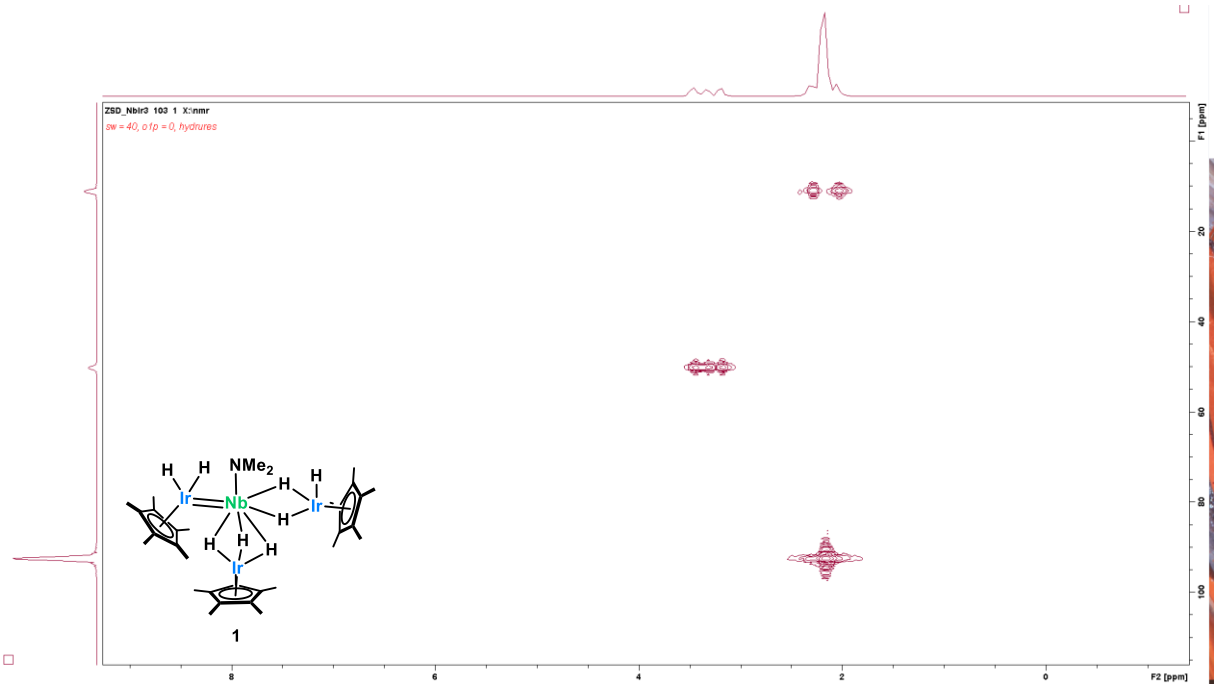


Figure S 5 : ^{1}H ^{13}C HSQC NMR spectrum of complex 1 in C_6D_6 (298K).

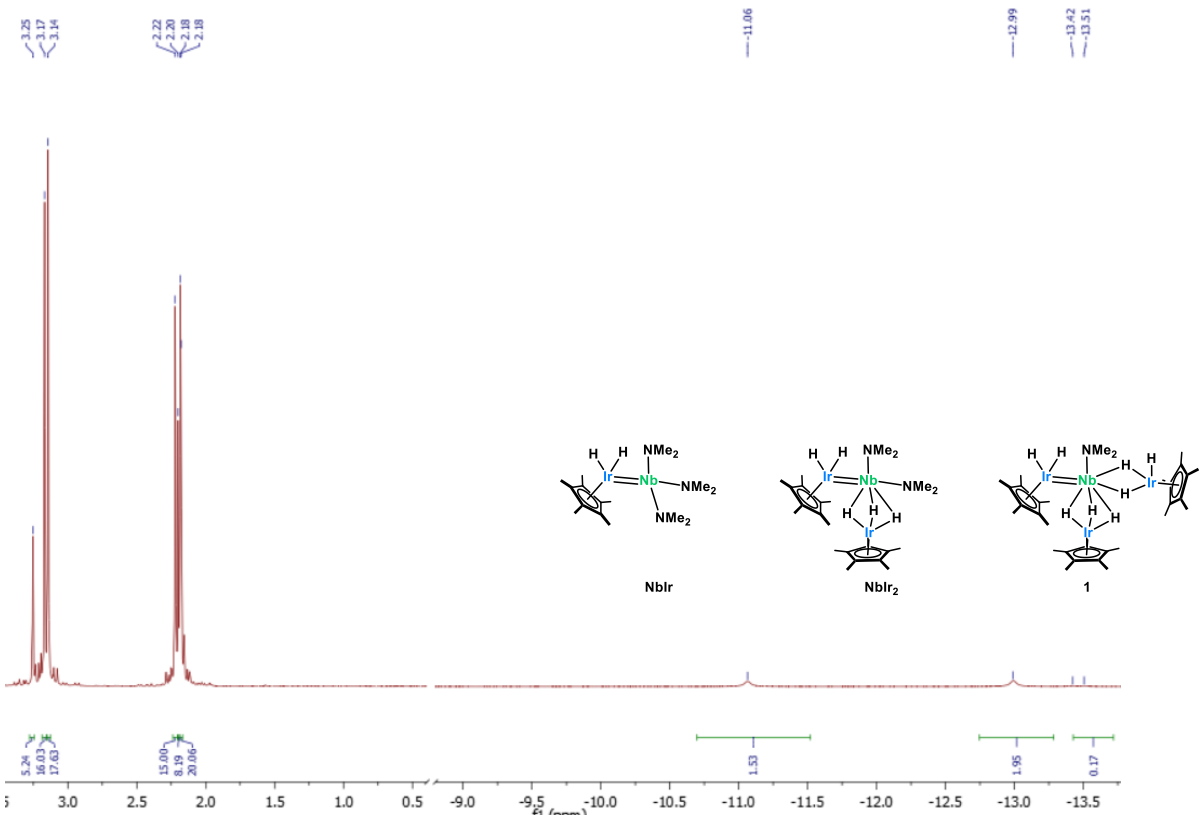


Figure S 6 : A representative ^{1}H NMR spectrum (C_6D_6, 298K, 300 MHz) during the attempted synthesis of lower Nb:Ir stoichiometry complexes. This spectrum was obtained from the addition of one equivalent of Cp^*IrH_4 to one equivalent of $Nb(NMe_2)_5$. New ^{1}H NMR signals emerge in the hydride region, confirming the formation of several Nb-Ir species. Unfortunately the 1:1 Nb:Ir stoichiometry complex could not be isolated cleanly as the reaction leads to several species of various stoichiometry with similar solubility.

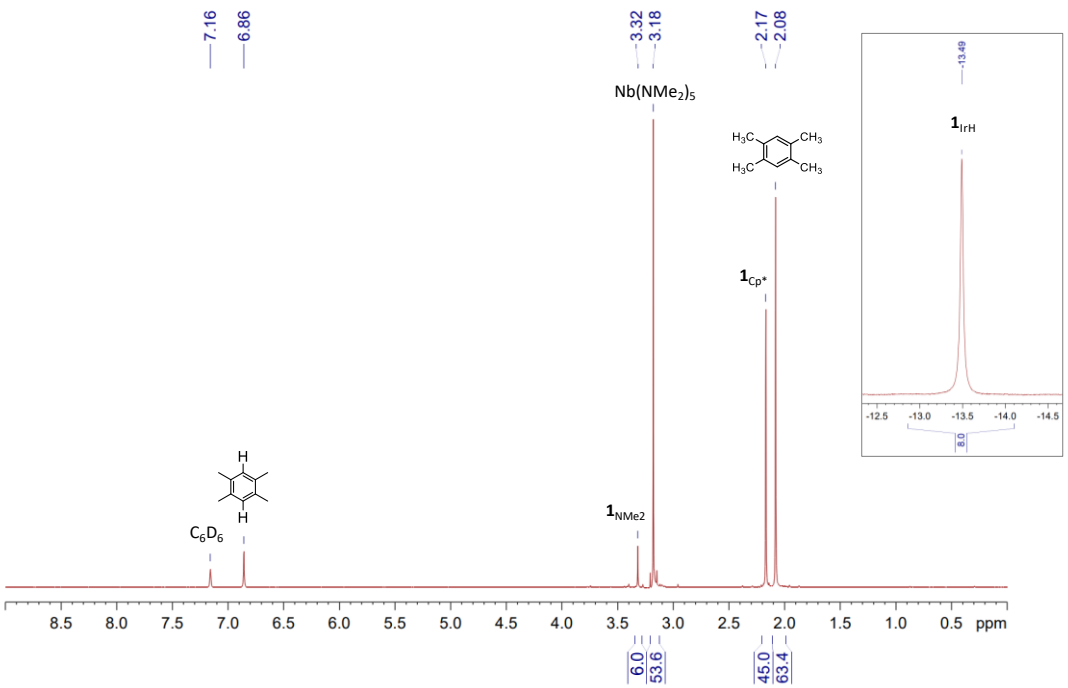


Figure S 7 : Representative ^{1}H NMR spectrum (C_6D_6, 298K, 300 MHz) of the attempted reaction between complex 1 and $Nb(NMe_2)_5$ at 70°C, showing no reaction. Durene is used as internal standard. Neither increasing the temperature to 100°C nor employing a larger excess of $Nb(NMe_2)_5$ resulted in any observable reactivity.

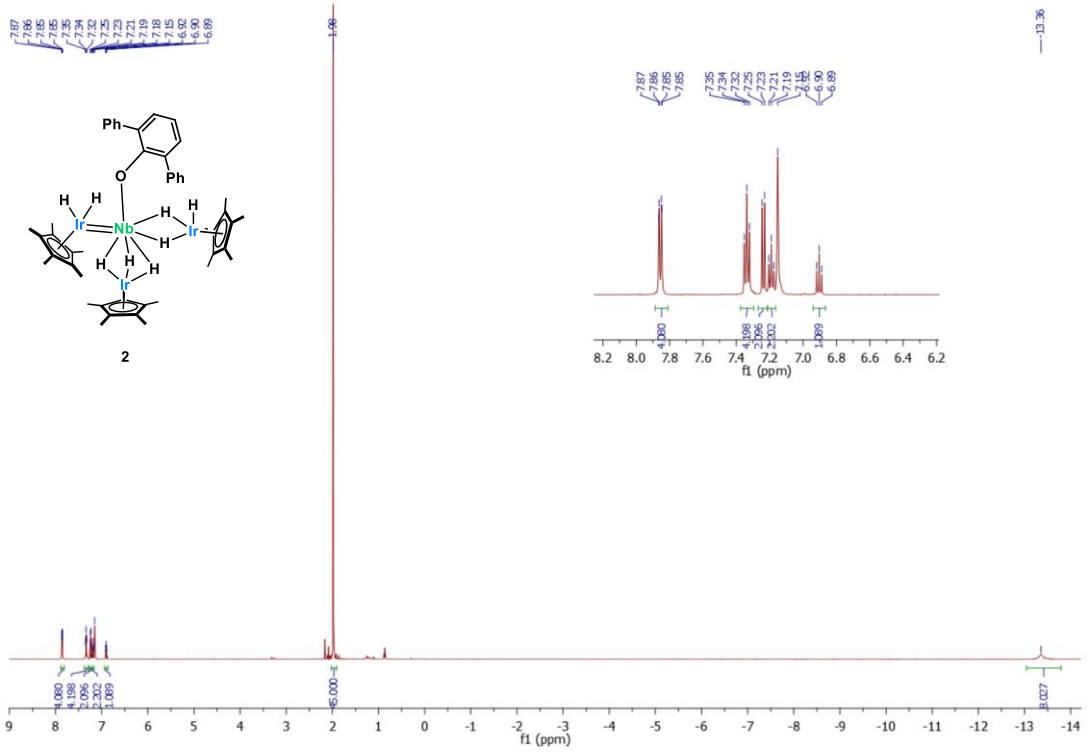


Figure S 8 : ^{1}H NMR spectrum of complex 2 in C_6D_6 (298K, 500 MHz).

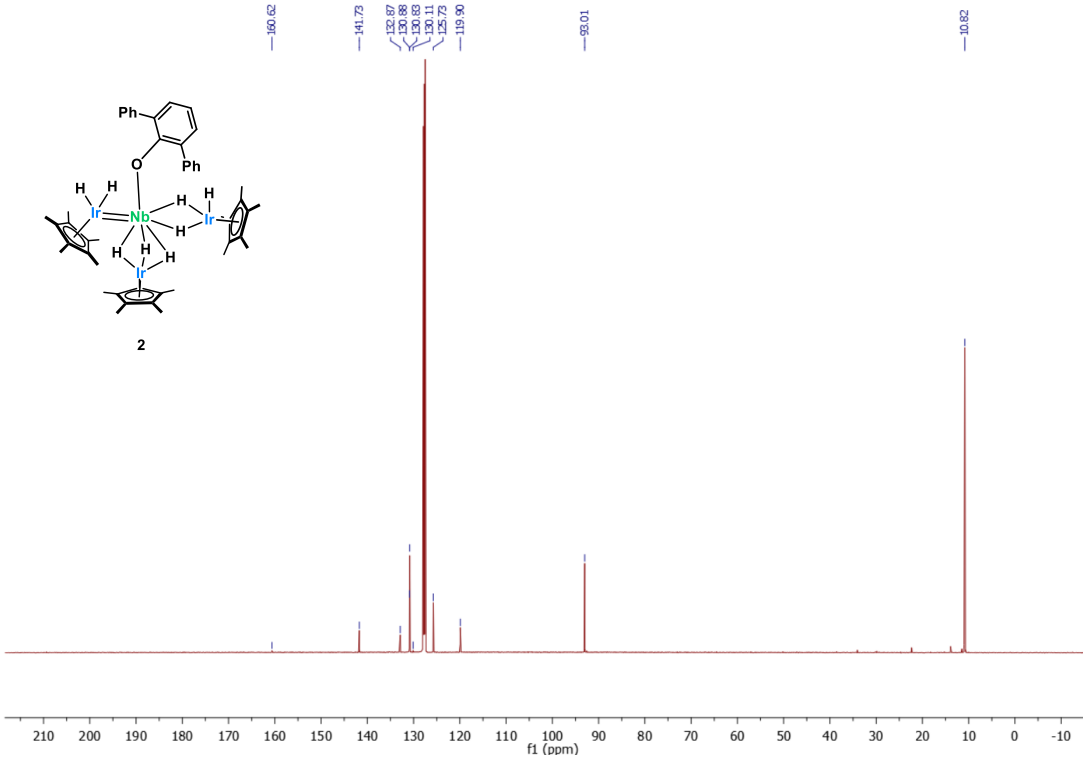


Figure S 9 : ^{13}C NMR spectrum of compound 2 in C_6D_6 (298K, 126 MHz).

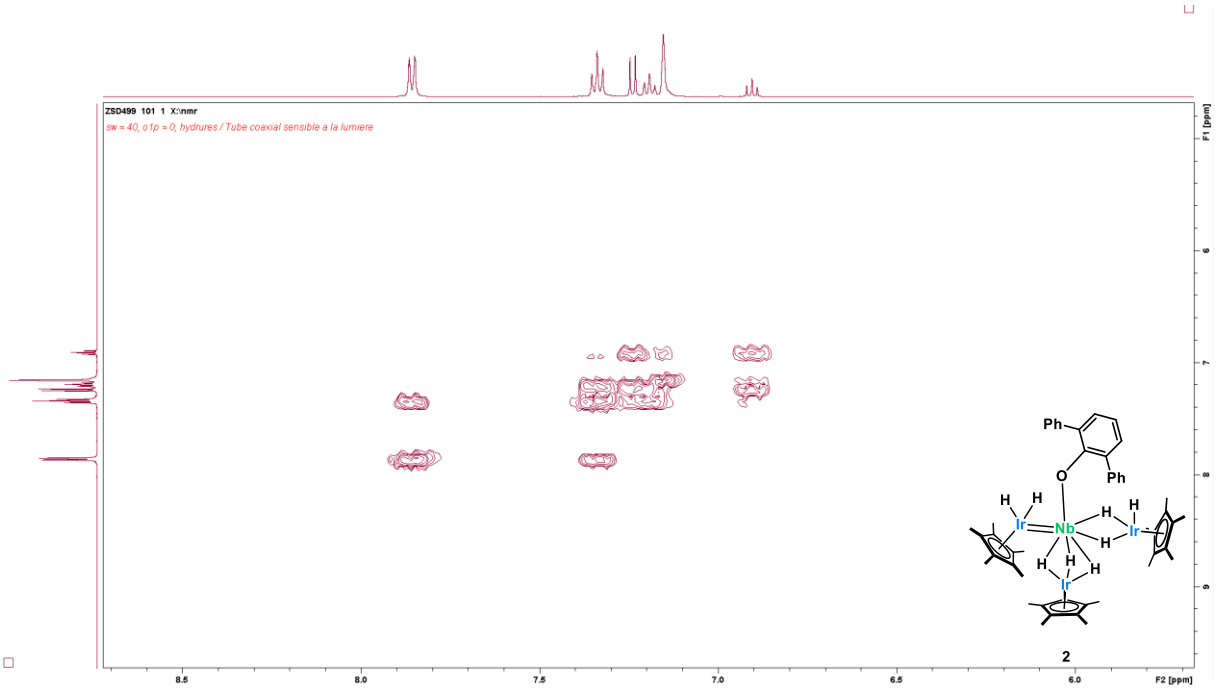


Figure S 10 : ^{1}H-^{1}H COSY NMR spectrum of compound 2 in C_6D_6 (298K, 500 MHz). Spectra represented along direct and indirect axes are external projections of the 1D spectrum collected on the same sample.

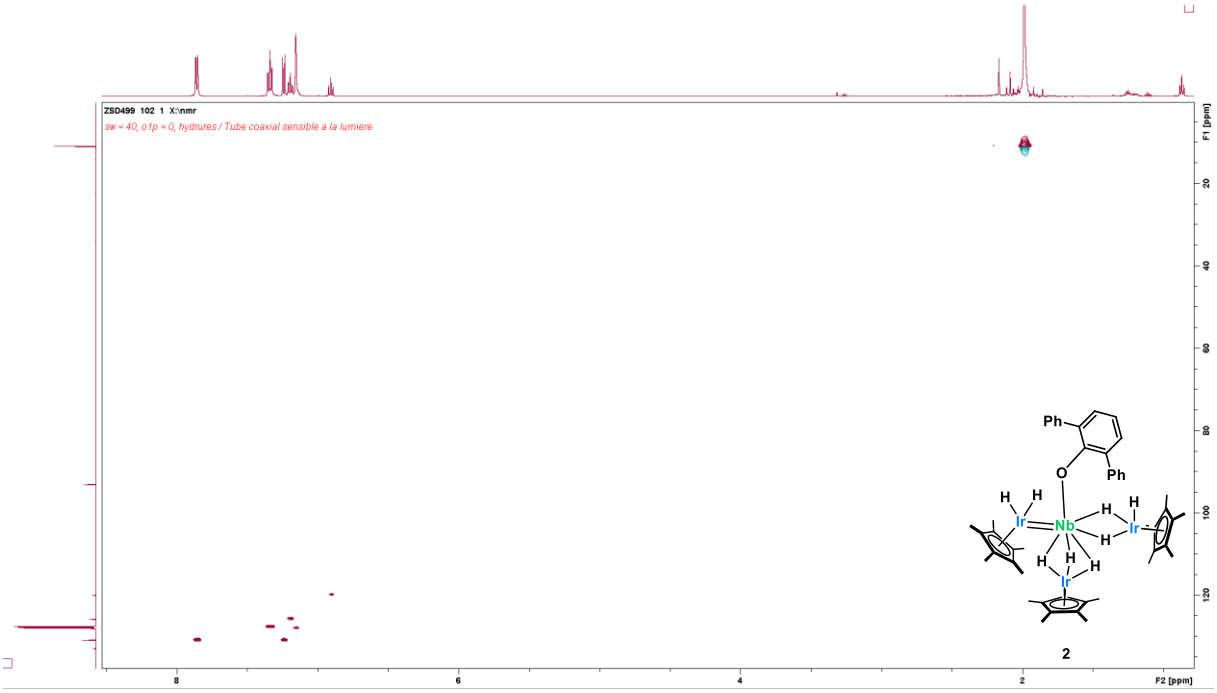


Figure S 11: ^{1}H-^{13}C HSQC NMR spectrum compound 2 in C_6D_6 (298K, 500 MHz). Spectra represented along direct and indirect axes are external projections of 1D spectra collected on the same sample.

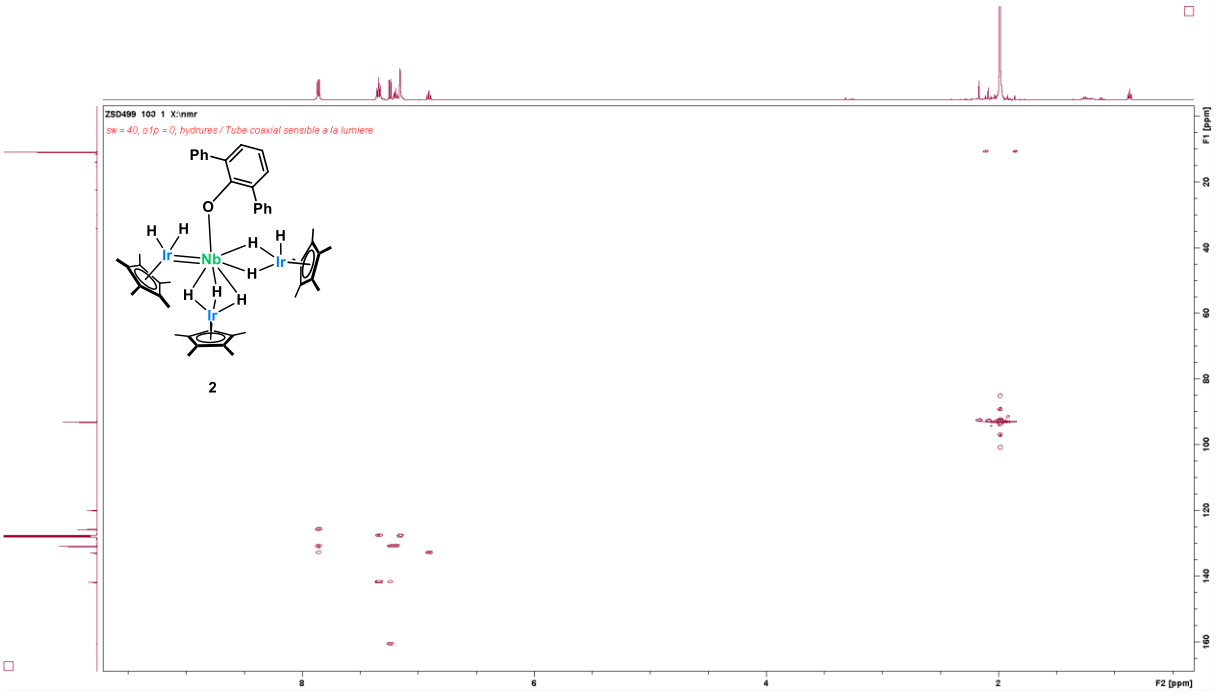


Figure S 12 : ^{1}H-^{13}C HMBC NMR spectrum of compound 2 in C_6D_6 (298K, 500 MHz). Spectra represented along direct and indirect axes are external projections of 1D spectra collected on the same sample.

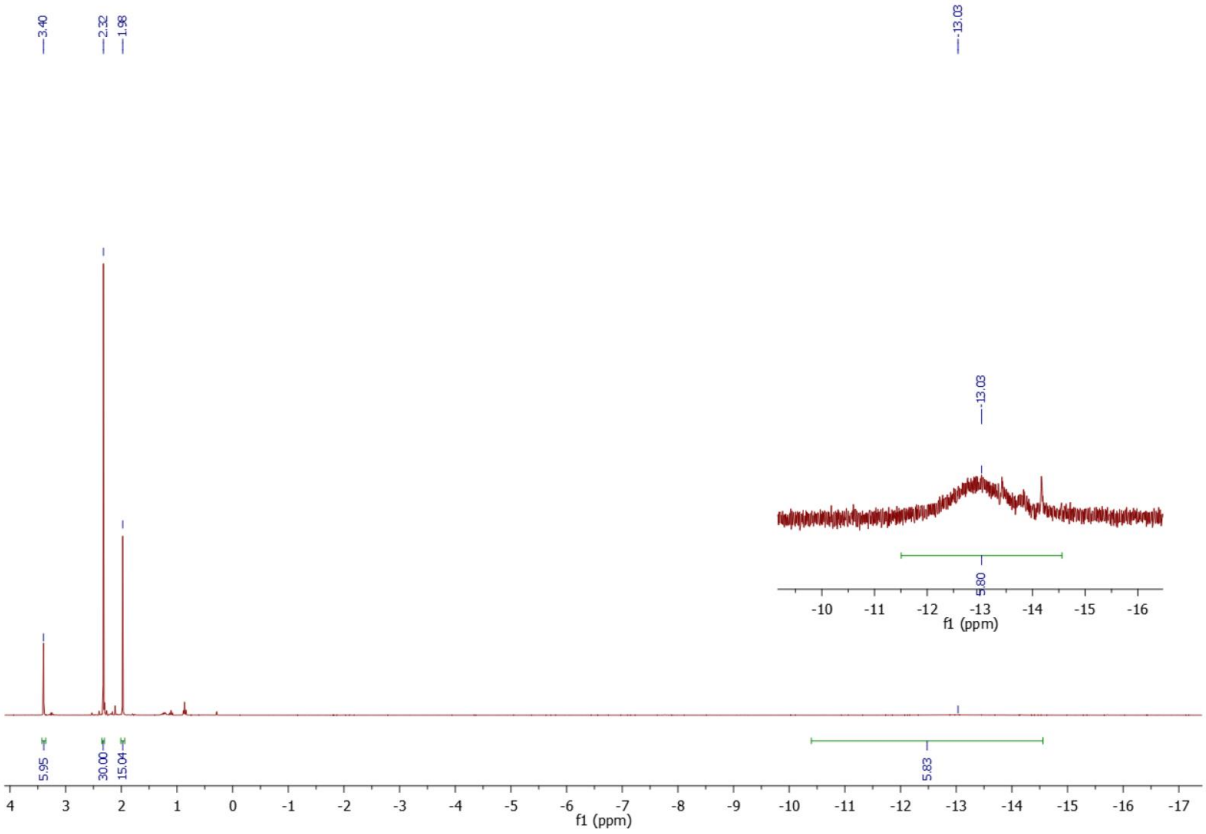


Figure S 13 : ^{1}H NMR spectrum of complex 3 in C_6D_6 (298K, 500 MHz) with inset showing a zoomed-in portion of the hydride region.

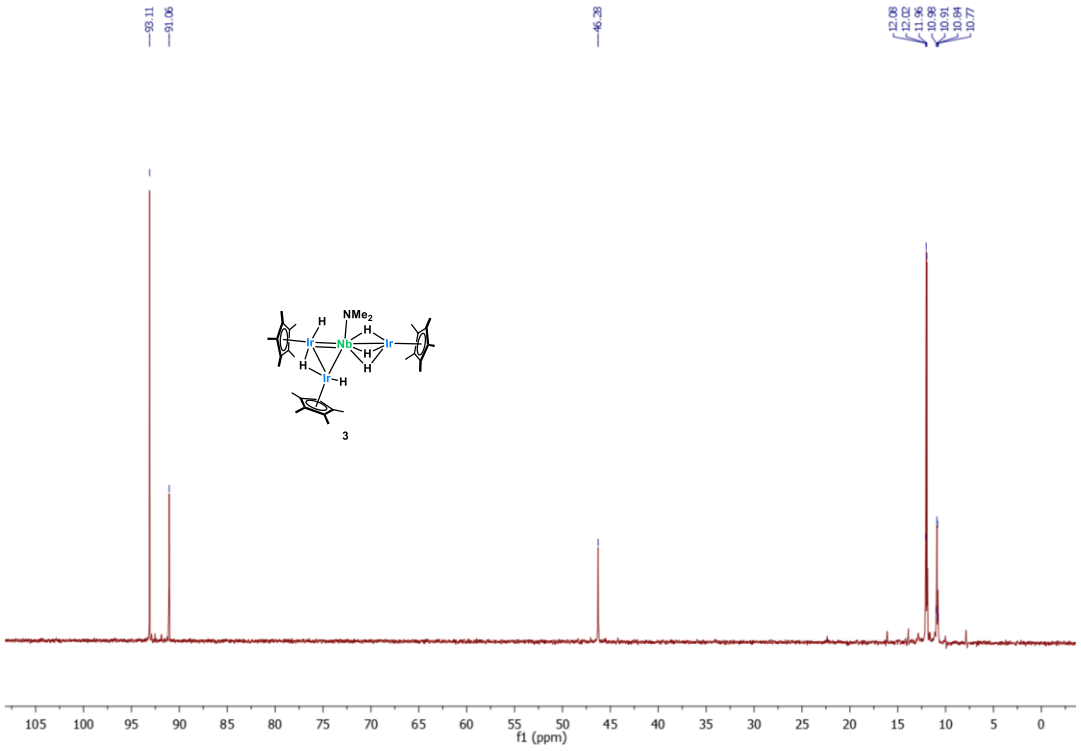


Figure S 14 : ^{13}C NMR spectrum of complex 3 in C_6D_6 (298K, 126 MHz). Note that this spectrum was accidentally collected without ^{1}H decoupling and so the signals at 12 – 10 ppm, which are the methyl groups found of the Cp* ligands, appear as 1:3:3:1 quartets.

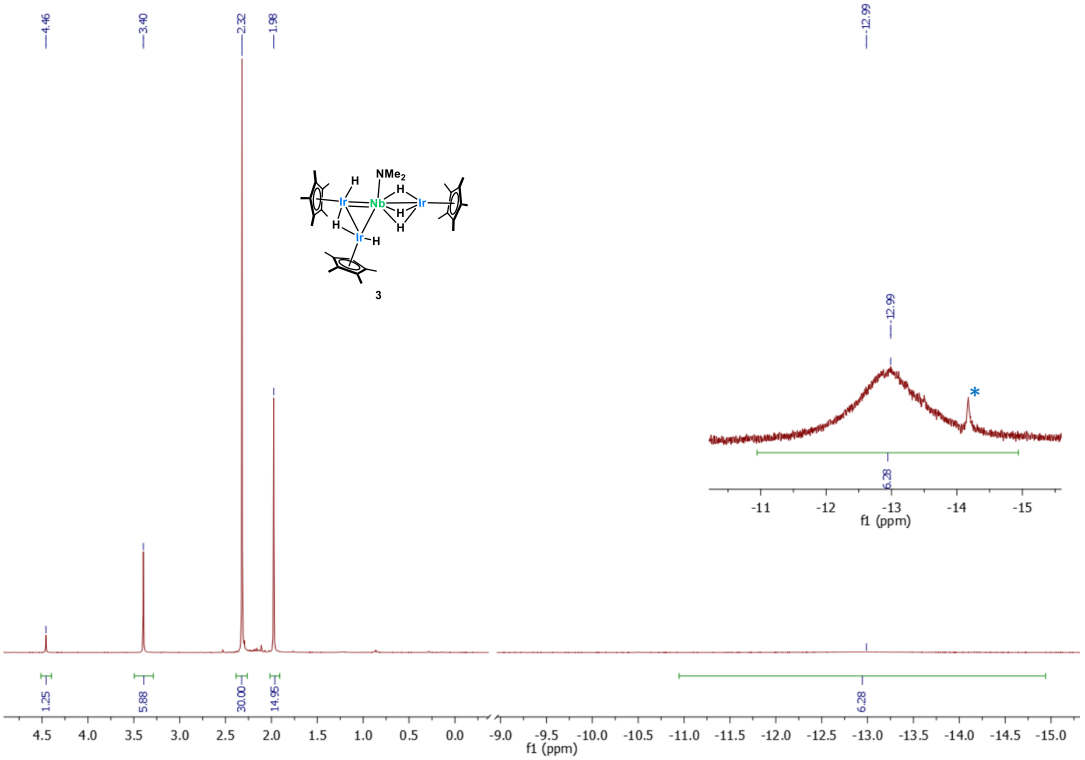


Figure S 15 : ^{1}H NMR spectrum of complex 3 in C_6D_6 (298K, 500 MHz) with the photolysis experiment is performed in a tube completely full of solvent. This allows for the detection of H_2 (signal at +4.46 ppm). The integral is low due to the presence of a small air bubble in the NMR tube and the low solubility of H_2 in benzene. Inset shows a zoomed-in portion of the spectrum focussing on the hydride region. Some complex 5 is present, as marked with a blue asterisk, coming from an impurity of Cp^*IrH_4 from the start of the experiment.

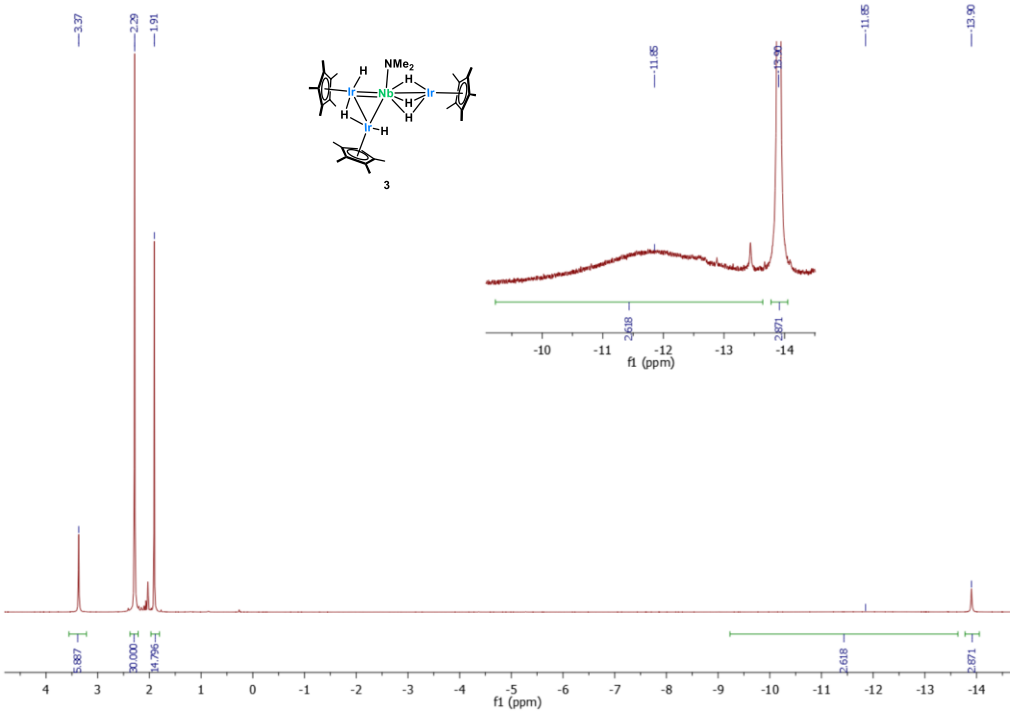


Figure S 16 : ^{1}H NMR spectrum of complex 3 in d_8-toluene recorded at -35°C (500 MHz). Inset shows a zoomed-in portion of the spectrum focussing on the hydride region where two signals can be observed.

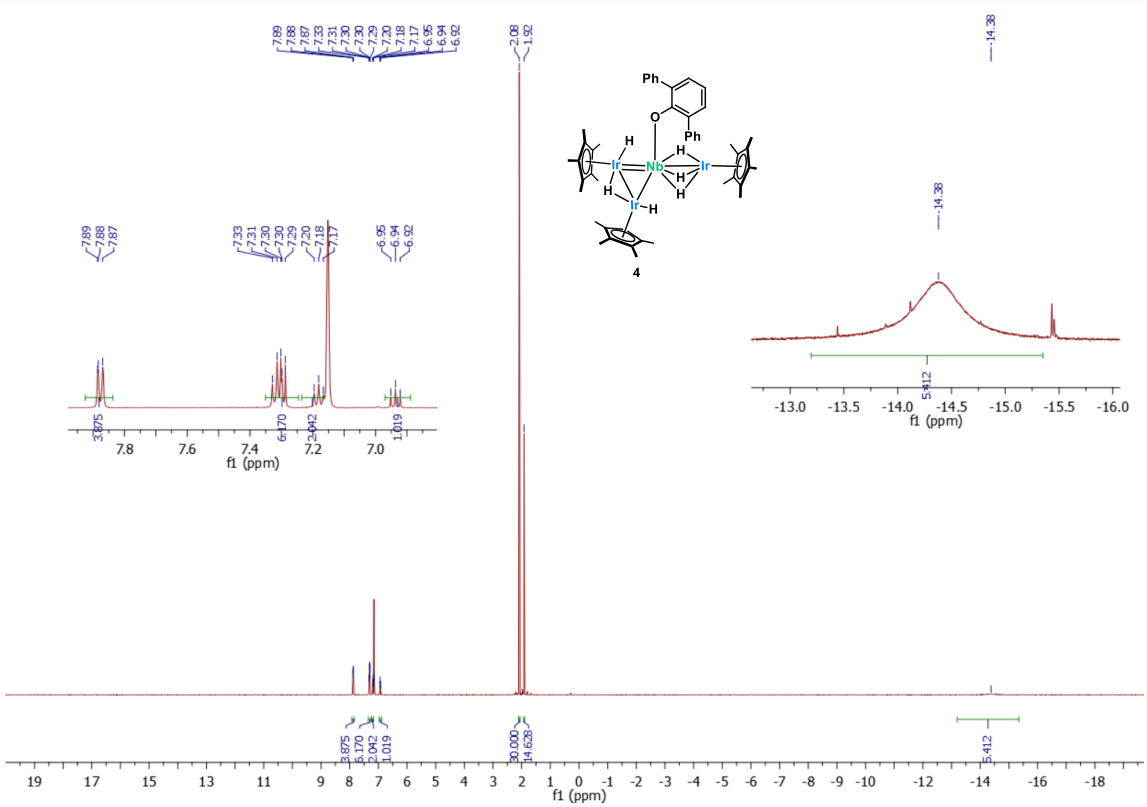


Figure S 17 : ^{1}H NMR spectrum of compound 4 in C_6D_6 (298K, 500 MHz).

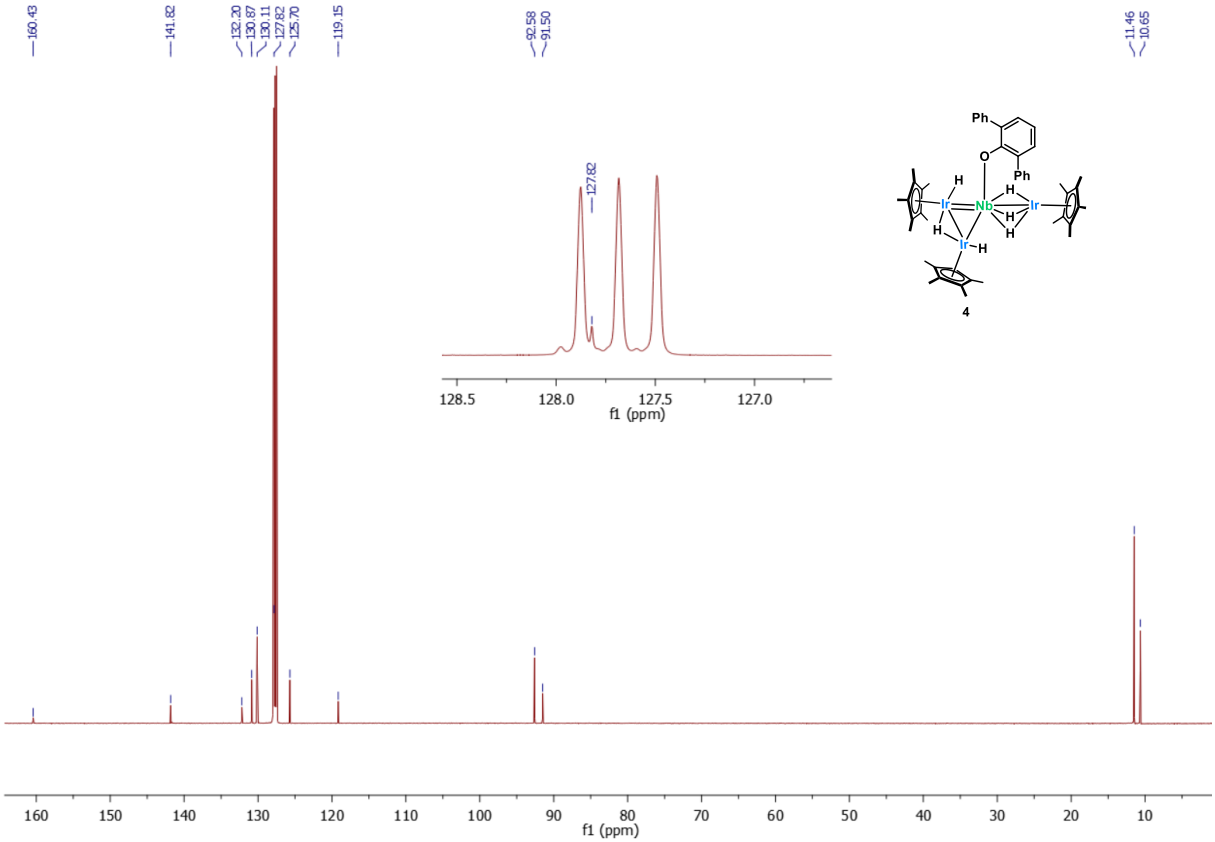


Figure S 18 : ^{13}C NMR spectrum of complex 4 in C_6D_6 (298K, 126 MHz).

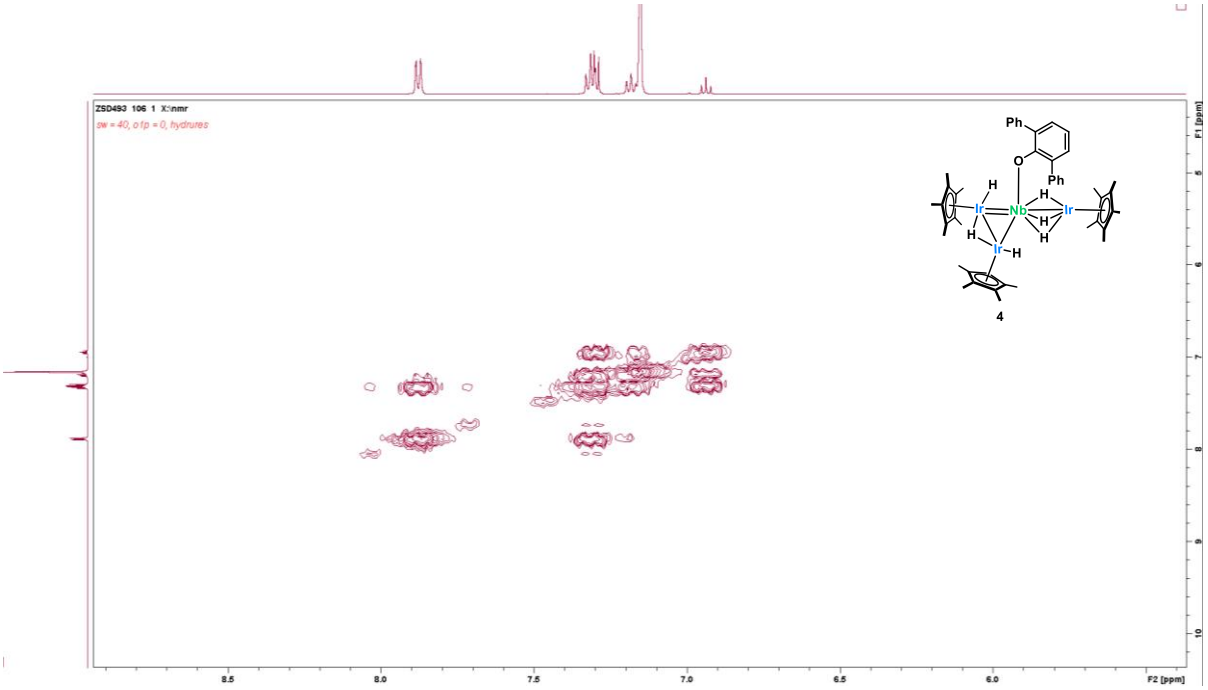


Figure S 19 : ^{1}H-^{1}H COSY NMR spectrum of compound 4 in C_6D_6 (298K, 500 MHz). Spectra represented along direct and indirect axes are external projections of the 1D spectrum collected on the same sample.

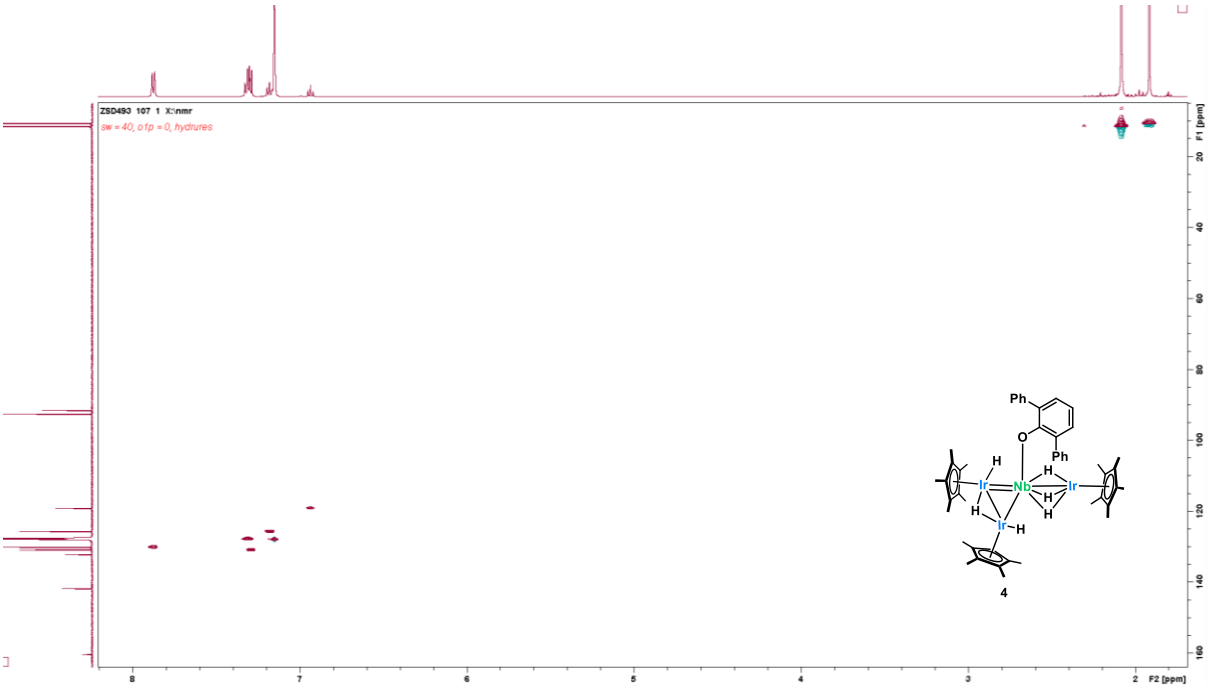


Figure S 20 : ^{1}H-^{13}C HSQC NMR spectrum of compound 4 in C_6D_6 (298K, 500 MHz). Spectra represented along direct and indirect axes are external projections of 1D spectra collected on the same sample.

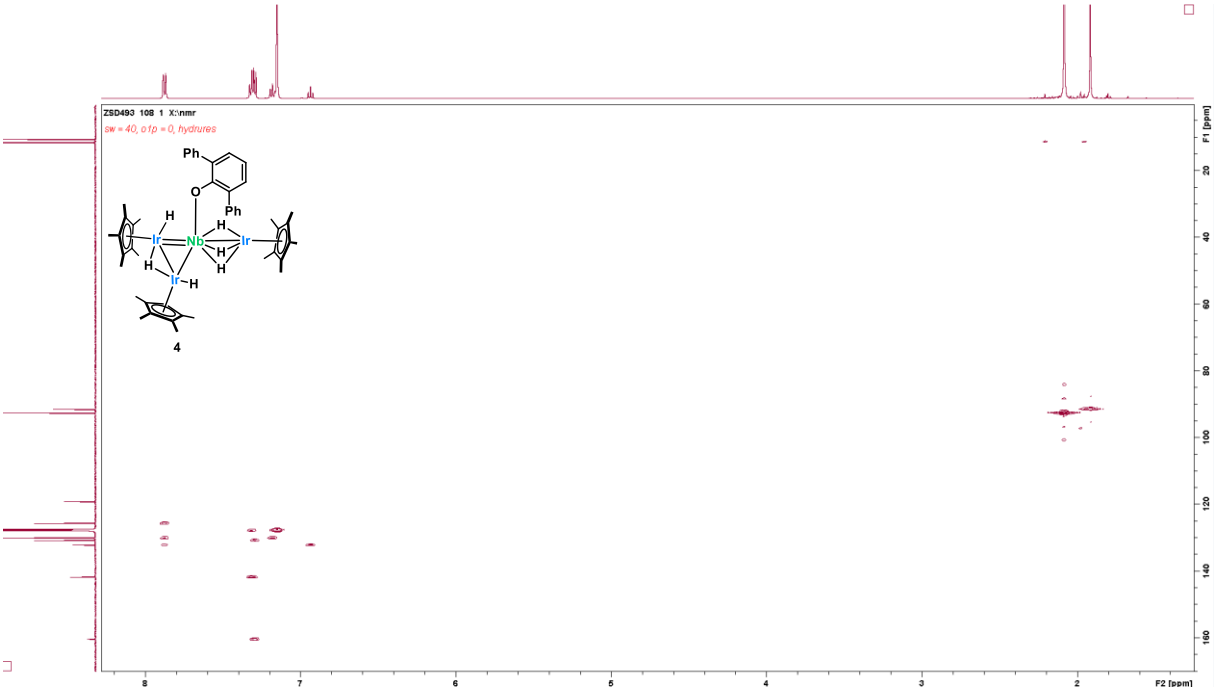


Figure S 21 : ^{1}H-^{13}C HMBC NMR spectrum of compound 4 in C_6D_6 (298K, 500 MHz). Spectra represented along direct and indirect axes are external projections of 1D spectra collected on the same sample.

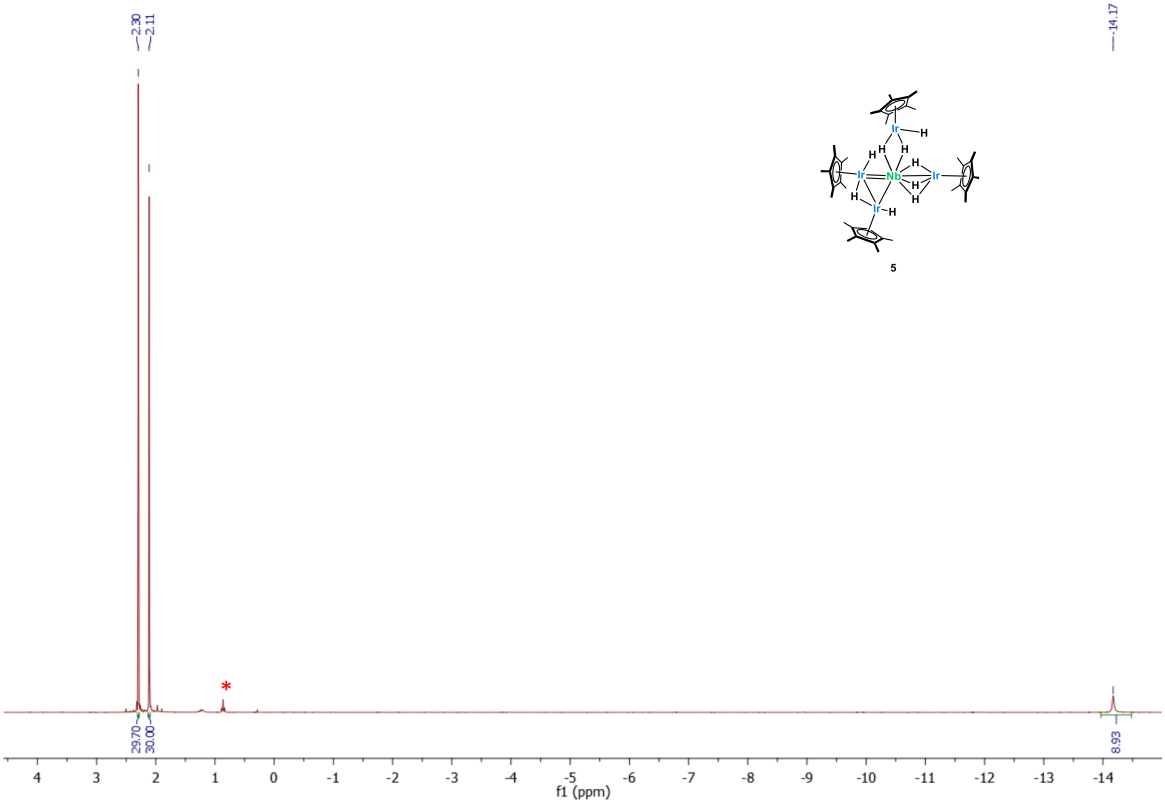


Figure S 22 : ^{1}H NMR spectrum of compound 5 in C_6D_6 (298K, 500 MHz). Some pentane can be observed and is marked with a red asterisk.

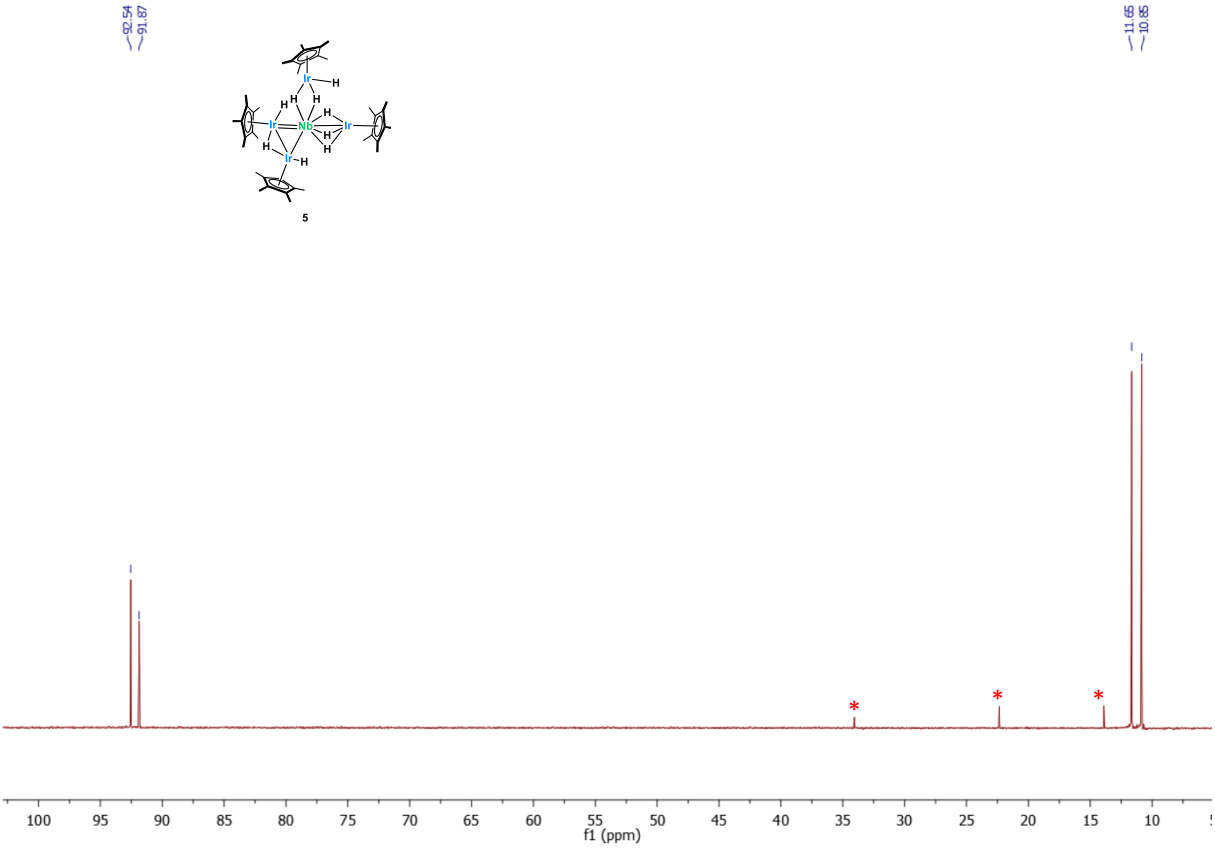


Figure S 23 : ^{13}C NMR spectrum of complex 5 in C_6D_6 (298K, 126 MHz). Some pentane is present in the spectrum and is marked with a red asterisk.

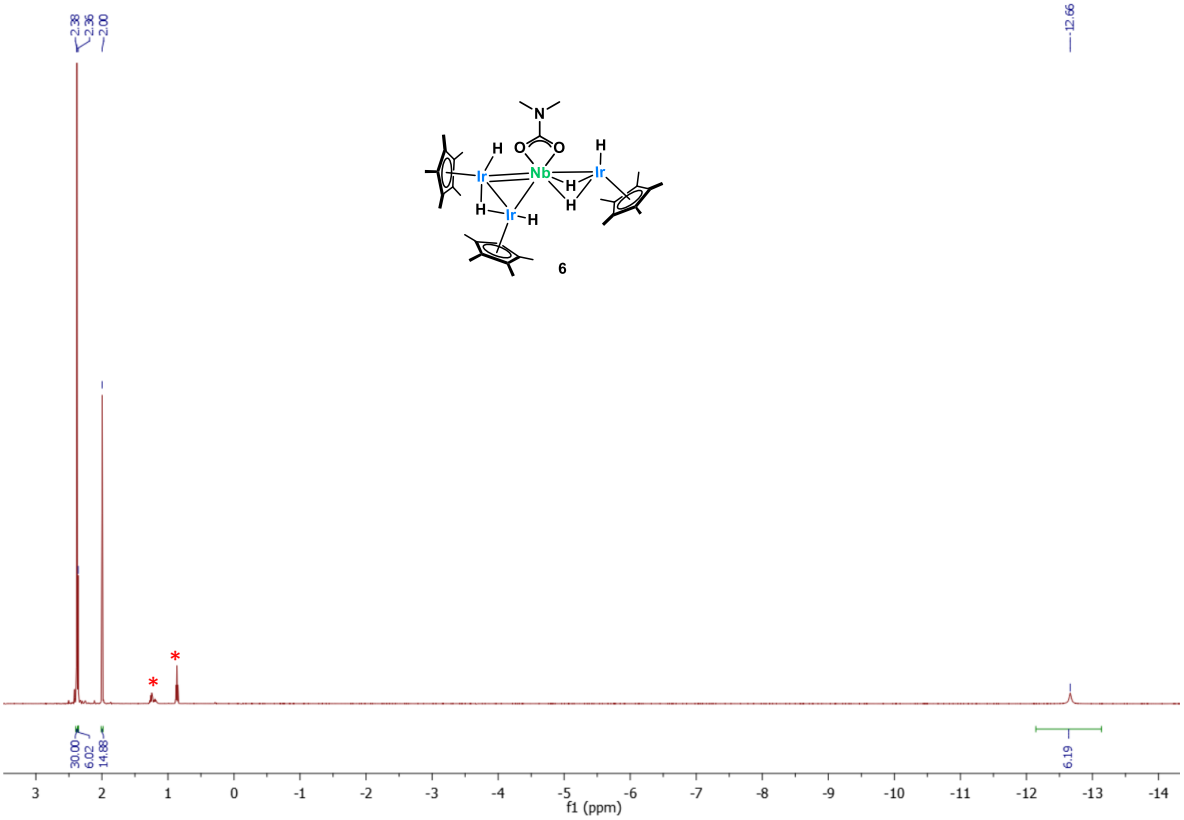


Figure S 24 : ^{1}H NMR spectrum of compound 6 in C_6D_6 (298K, 500 MHz). Some pentane can be observed and is marked with a red asterisk.

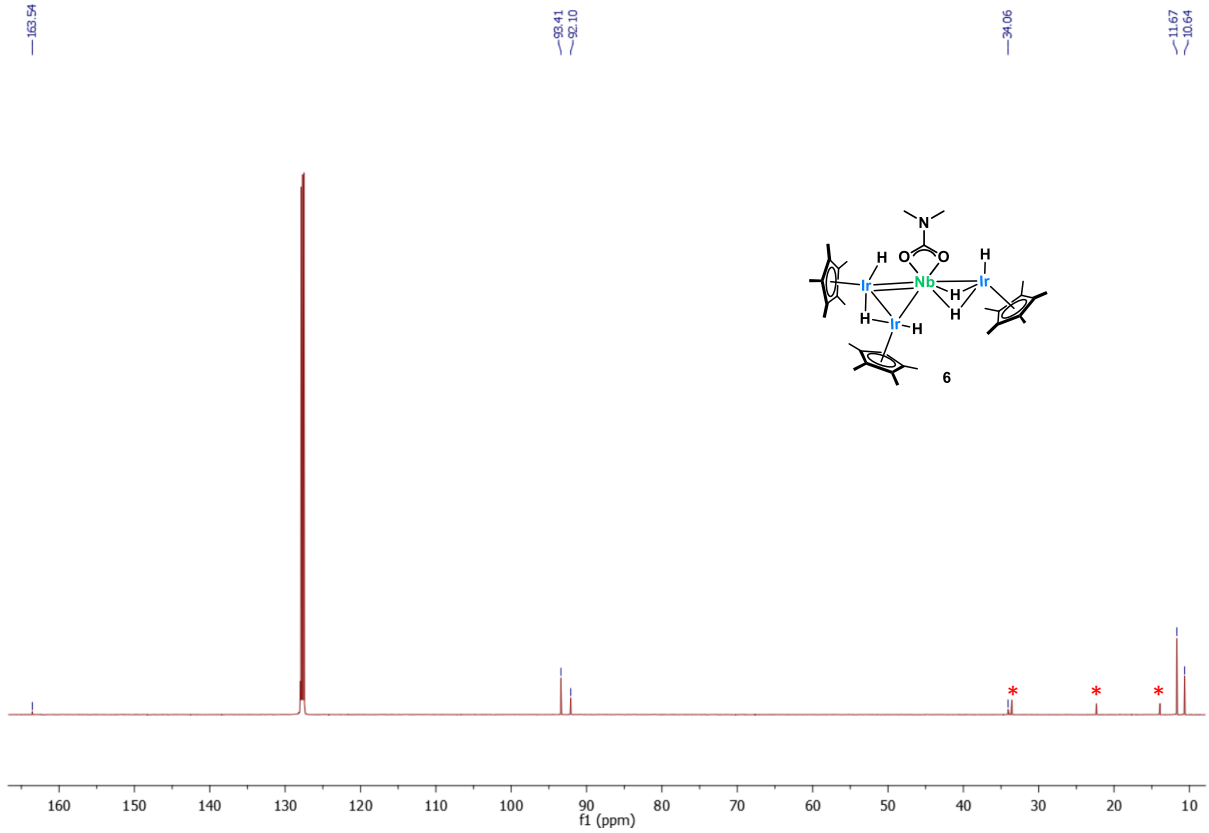


Figure S 25 : ^{13}C NMR spectrum of compound 6 in C_6D_6 (298K, 500 MHz). Some pentane can be observed and is marked with a red asterisk.

DRIFT spectra

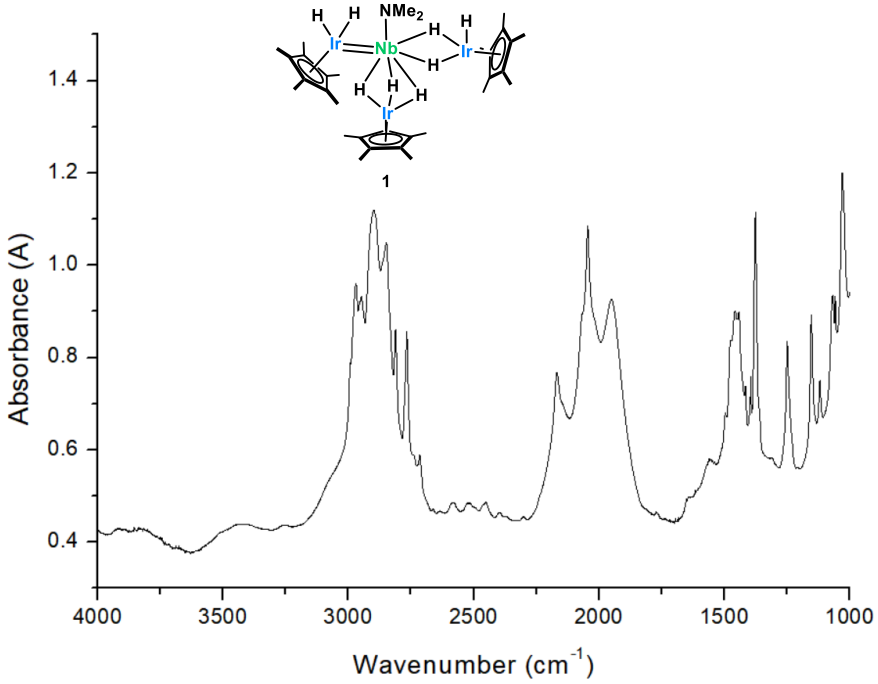


Figure S 26 : DRIFT spectrum of complex 1, diluted in KBr.

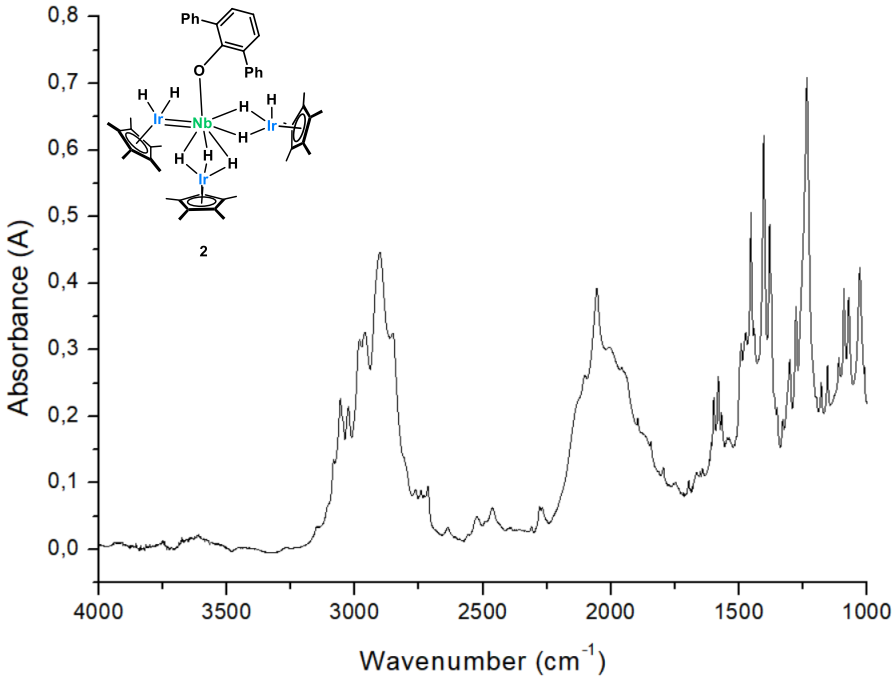


Figure S 27 : DRIFT spectrum of complex 2, diluted in KBr.

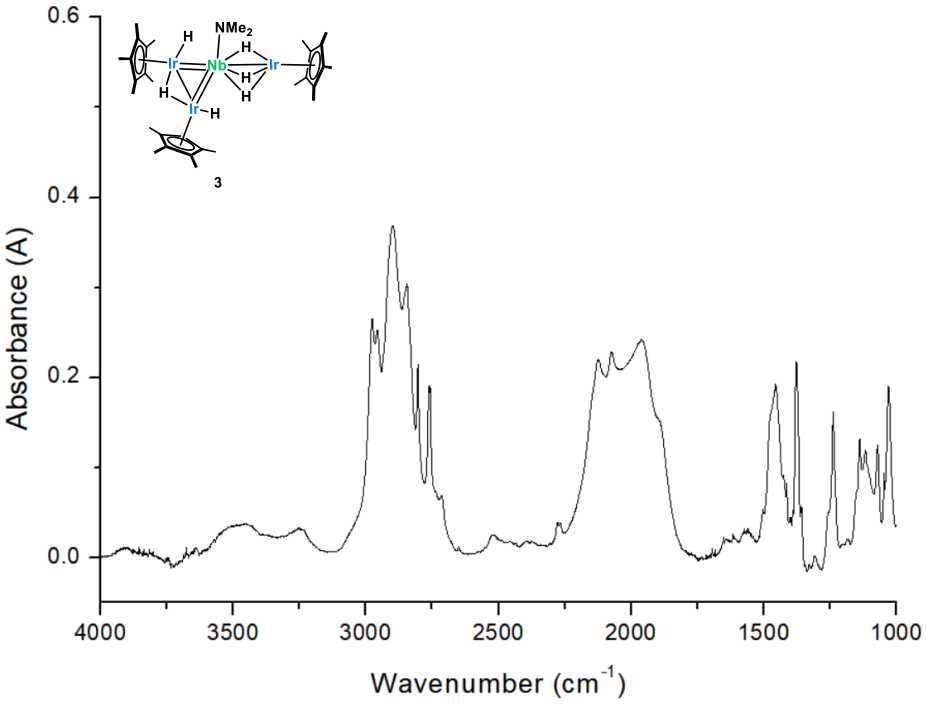


Figure S 28 : DRIFT spectrum of complex 3, diluted in KBr.

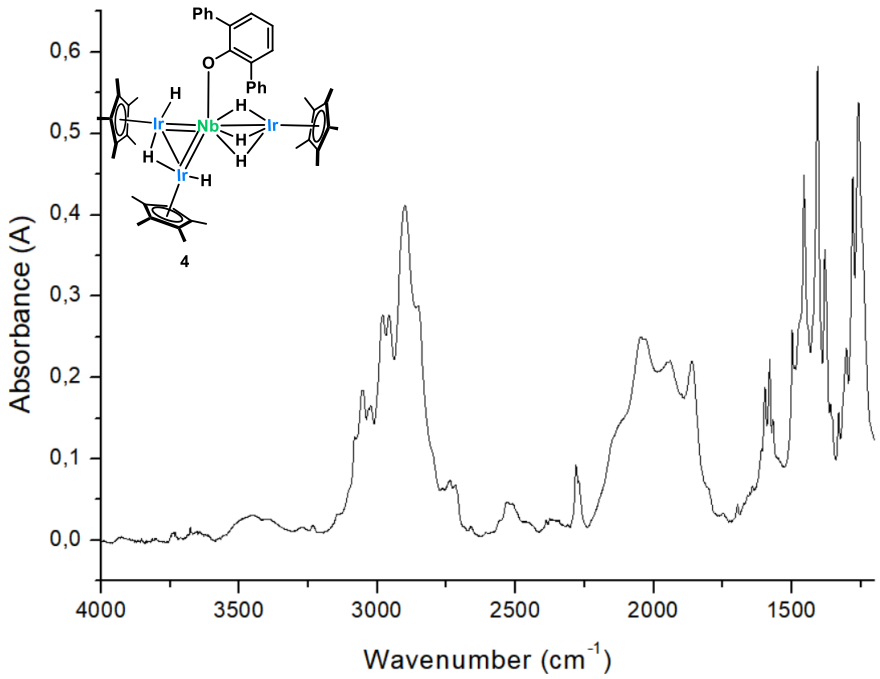


Figure S 29 : DRIFT spectrum of complex 4, diluted in KBr.

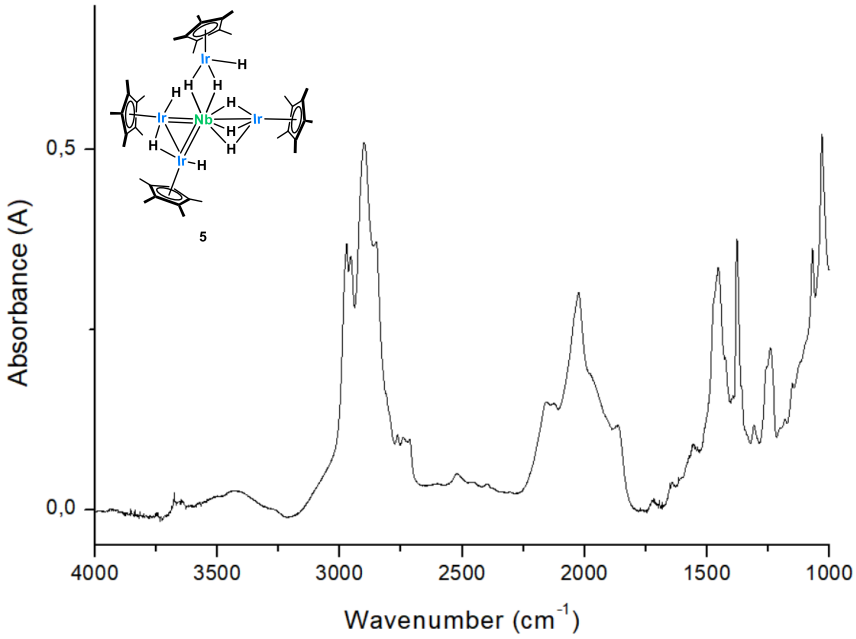


Figure S 30 : DRIFT spectrum of complex 5, diluted in KBr.

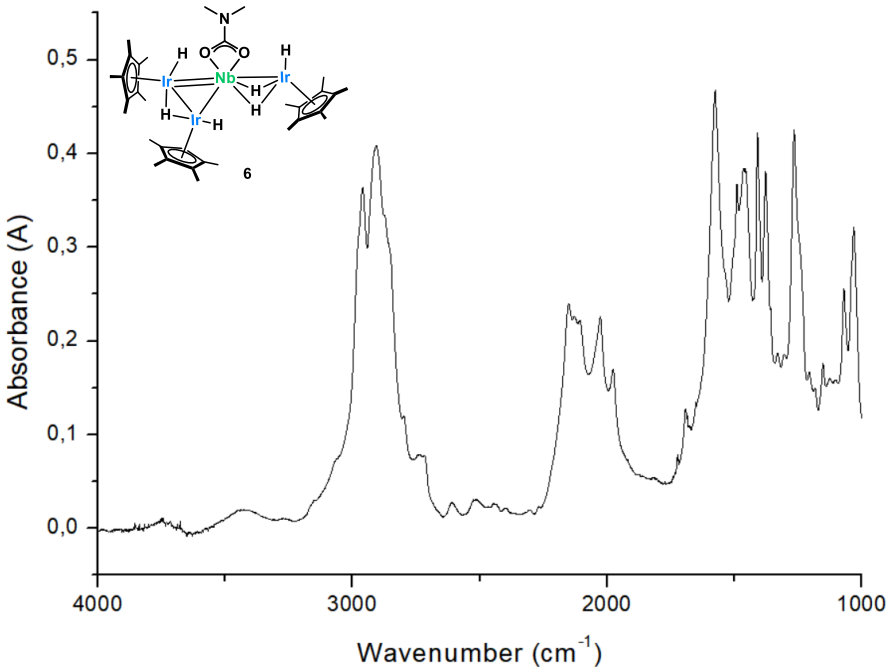


Figure S 31 : DRIFT spectrum of complex 6, diluted in KBr.

UV-Vis spectra

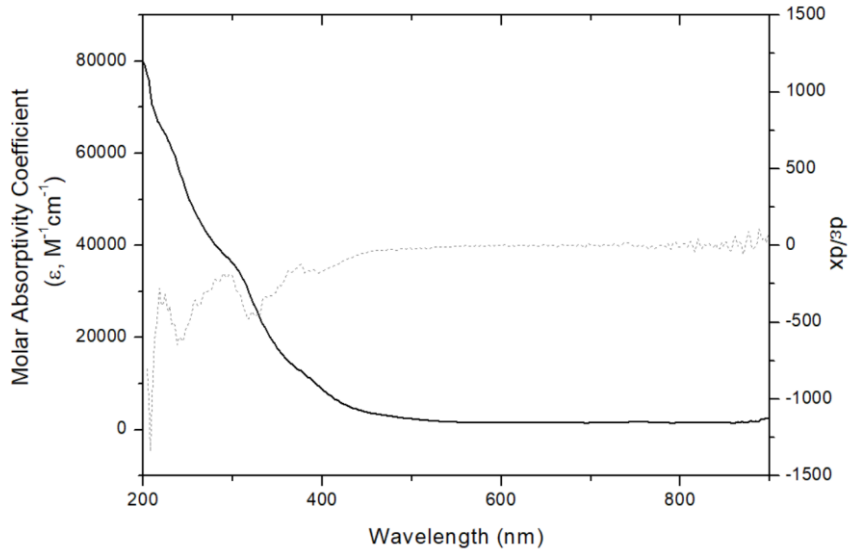


Figure S 32 : UV-Vis spectrum of complex 1 in pentane (27.8 µM solution). Derivative trace is plotted in gray.

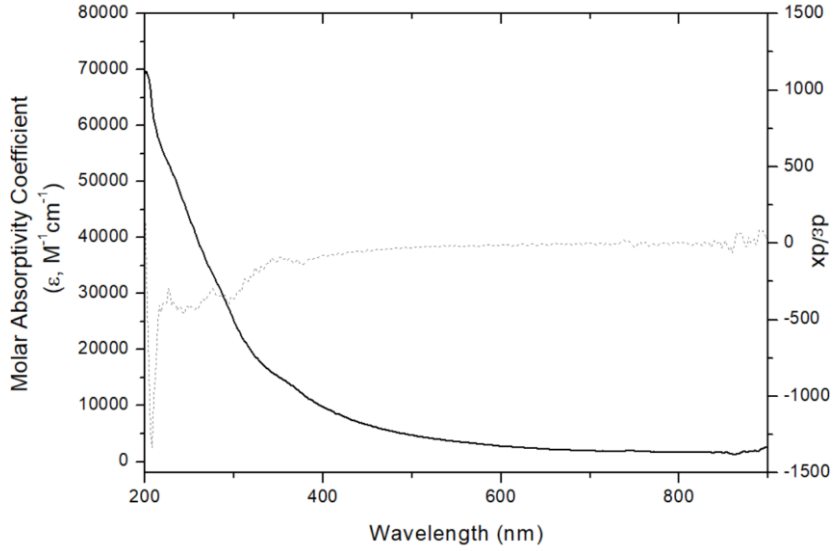


Figure S 33 : UV-Vis spectrum of complex 3 in pentane (27.8 µM solution). Derivative trace is plotted in gray.

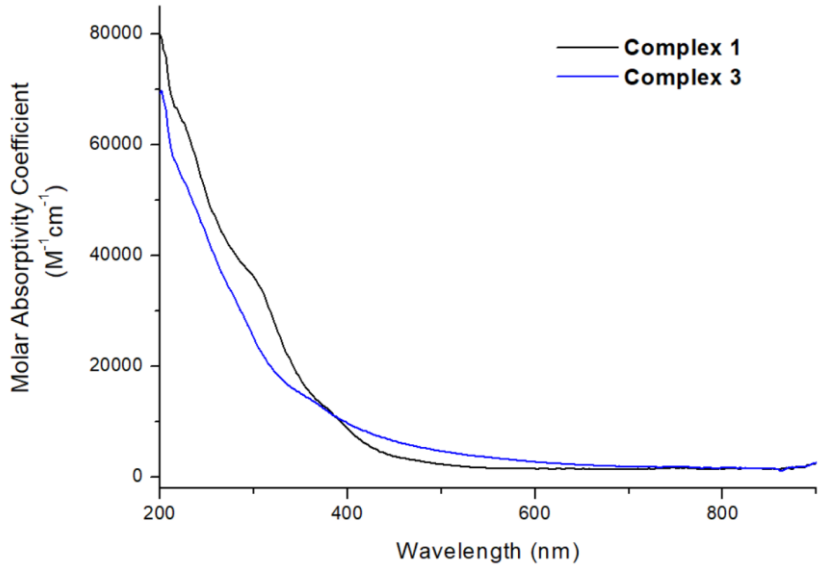


Figure S 34 : An overlay of the UV-Vis spectra of complexes 1 and 3 (in pentane, M = 27.8 µM solution) showing how the absorption profile changes after irradiation with visible light.

X-ray diffraction data

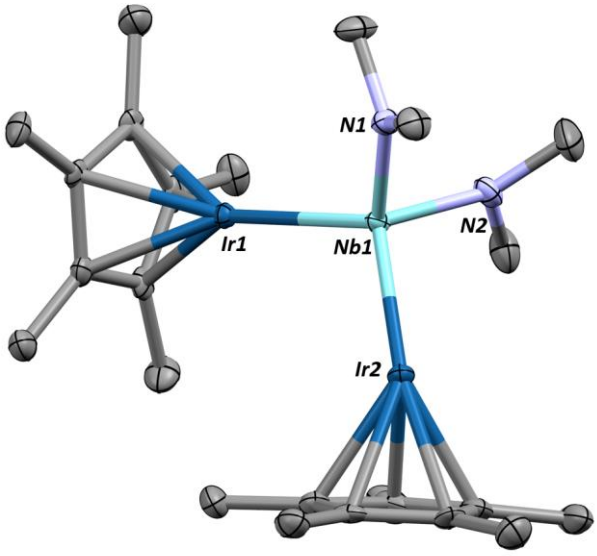


Figure S 35 : The single crystal X-ray diffraction structure of complex $(Cp^*IrH_3)(Cp^*IrH_2)Nb(NMe_2)_2$ which was found during initial synthesis attempts of complex 1 with lower stoichiometry, shown with hydrogens removed for clarity and thermal ellipsoids at 50%. Structural parameters are as follows (distances in Å and angles in °): Nb1 – N1 = 1.9810(4), Nb1 – N2 = 2.000(5) Nb1 – Ir1 = 2.6696(6) (FSR = 1.02), Nb1 – Ir2 = 2.4284(6) (FSR = 0.93), $<Cp^*_{Centroid}$ – Ir1 – Nb1 = 177.75, $<Cp^*_{Centroid}$ – Ir2 – Nb1 = 152.87, τ_4 = 0.94.

X-ray crystallography tables

Table S1 : X-ray crystallography data collection and refinement parameters for compounds 1-6.

Compound	**1**	**2**	**3**	**4**	**5**	**6**
Formula	$C_{32}H_{51}NNbIr_3$	$C_{53}H_{70}Ir_3NbO$	$C_{32}H_{51}Ir_3NNb$	$C_{53}H_{70}Ir_3NbO$	$C_{40}H_{60}Ir_4Nb$	$C_{38}H_{63}Ir_3NNbO_2$
$D_{calc.}$/ g cm^{-3}	2.130	1.857	2.091	1.826	2.177	1.995
μ/mm^{-1}	11.741	8.247	23.914	16.948	25.749	9.975
Formula Weight	1119.24	1392.700	1119.24	1392.60	1402.59	1235.40
Colour	red	black	dark orange	dark brown	black	brown
Shape	block-shaped	block-shaped	plate-shaped	plate-shaped	block-shaped	needle-shaped
Size/mm^3	0.26×0.20×0.15	0.25×0.21×0.16	0.18×0.12×0.05	0.16×0.08×0.03	0.17×0.06×0.05	0.27×0.05×0.04
T/K	100.0(4)	100.0(3)	100.0(2)	100.02(10)	100.02(12)	100.00(11)
Crystal System	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic	triclinic
Space Group	$P2_1/c$	$P2_1/c$	$P2_12_12_1$	$P2_1/c$	$P2_1/n$	P-1
a/Å	12.27350(10)	16.3515(3)	12.54910(10)	18.62790(10)	12.7793(2)	11.1224(3)
b/Å	10.28130(10)	12.1117(2)	13.87850(10)	14.23730(10)	24.6740(3)	11.6146(3)
c/Å	27.6692(2)	26.2377(5)	20.41610(10)	19.74350(10)	13.8521(2)	16.8916(4)
α/°	90	90	90	90	90	73.274(2)
β/°	91.5220(10)	106.515(2)	90	104.6860(10)	101.4910(10)	86.167(2)
γ/°	90	90	90	90	90	79.895(2)
V/Å^3	3490.28(5)	4981.86(16)	3555.72(4)	5065.13(6)	4280.25(11)	2057.05(9)
Z	4	4	4	4	4	2
Z'	1	1	1	1	1	1
Wavelength/Å	0.71073	0.71073	1.54184	1.54184	1.54184	0.71073
Radiation	Mo K$_\alpha$	Mo K$_\alpha$	Cu K$_\alpha$	Cu K$_\alpha$	Cu K$_\alpha$	Mo K$_\alpha$
Θ_{min}/°	2.468	2.33	3.851	3.873	3.583	2.960
Θ_{max}/°	30.602	30.39	78.824	78.852	78.934	30.302
Measured Refl's.	70840	89765	67254	97566	80880	53801
Indep't Refl's	9323	12981	7433	10505	8988	10372
Refl's I≥2 σ(I)	8703	11131	7399	10302	8216	8279
R_{int}	0.0440	0.0628	0.0434	0.0383	0.0738	0.0653
Parameters	352	748	351	540	469	425
Restraints	0	1779	0	0	2856	0
Largest Peak	2.044	2.1016	2.911	2.438	2.741	2.987
Deepest Hole	-1.011	-2.1614	-0.909	-1.420	-3.177	-2.006
GooF	1.106	1.0287	1.049	1.097	1.069	1.144
wR_2 (all data)	0.0516	0.1377	0.0577	0.0694	0.1525	0.1214
wR_2	0.0508	0.1315	0.0576	0.0690	0.1495	0.1146
R_1 (all data)	0.0249	0.0798	0.0218	0.0255	0.0639	0.0696
R_1	0.0220	0.0646	0.0217	0.0250	0.0597	0.0500

Table S2 : X-ray crystallography data collection and refinement parameters for complex $(Cp^*IrH_3)(Cp^*IrH_2)Nb(NMe_2)_2$

Compound	**NbIr2**
Formula	$C_{24}H_{42}Ir_2N_2Nb$
$D_{calc.}$/ g cm^{-3}	1.995
μ/mm^{-1}	9.955
Formula Weight	835.90
Colour	dark red
Shape	block-shaped
Size/mm^3	0.30×0.20×0.16
T/K	100.00(10)
Crystal System	monoclinic
Space Group	$P2_1/c$
a/Å	10.1262(3)
b/Å	11.8871(3)
c/Å	23.4515(6)
α/°	90
β/°	99.588(2)
γ/°	90
V/Å^3	2783.45(13)
Z	4
Z'	1
Wavelength/Å	0.71073
Radiation type	Mo K_α
Θ_{min}/°	2.909
Θ_{max}/°	30.428
Measured Refl's.	63066
Indep't Refl's	7441
Refl's I≥2 σ(I)	6152
R_{int}	0.0778
Parameters	276
Restraints	6
Largest Peak	2.602
Deepest Hole	-2.876
GooF	1.047
wR_2 (all data)	0.0860
wR_2	0.0822
R_1 (all data)	0.0540
R_1	0.0396

References

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