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Supporting Information

Lability of Ta-NHC adducts as a Synthetic Route Towards Heterobimetallic Ta/Rh Complexes

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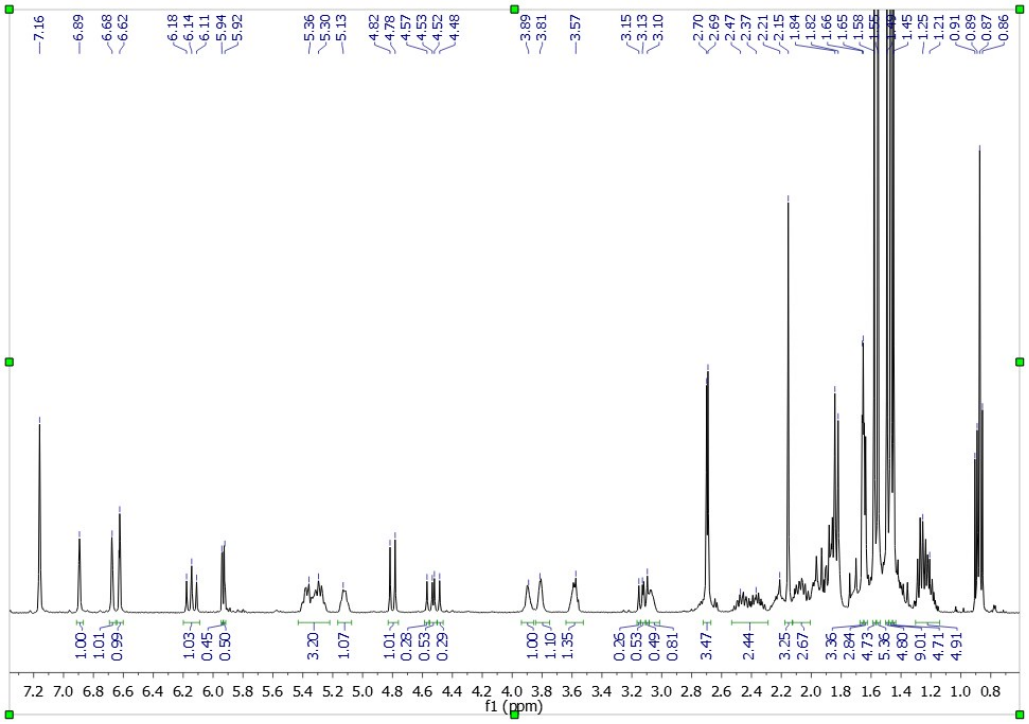


Figure S2. ^{13}C $\{^{1}H\}$ NMR spectrum of the trimetallic complex **2** (100 MHz, C_6D_6, 296 K).

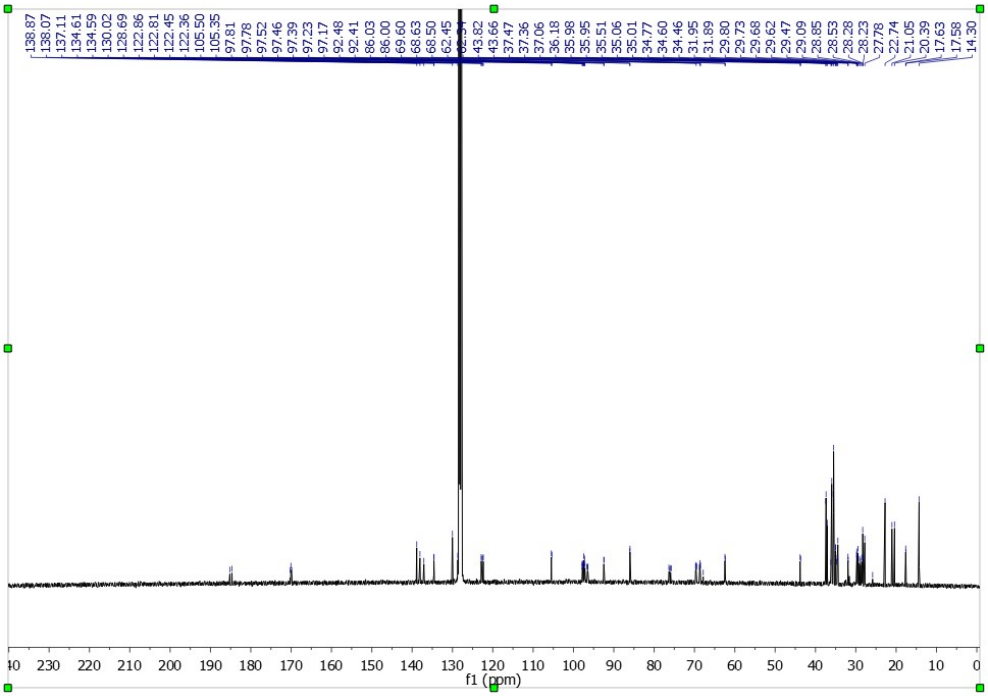


Figure S3. ^{1}H-^{1}H COSY NMR spectrum of the trimetallic complex **2** (400 MHz, C_6D_6, 296 K).

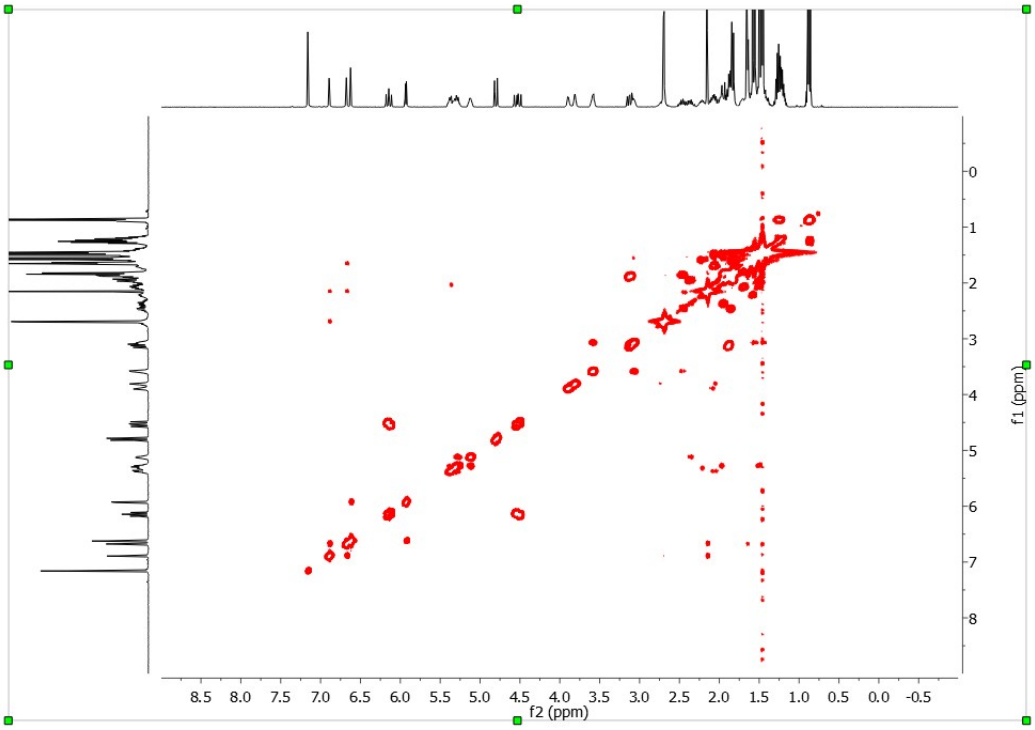


Figure S4. ^{1}H-^{13}C HSQC NMR spectrum of the trimetallic complex **2** (100 MHz, C_6D_6, 296 K).

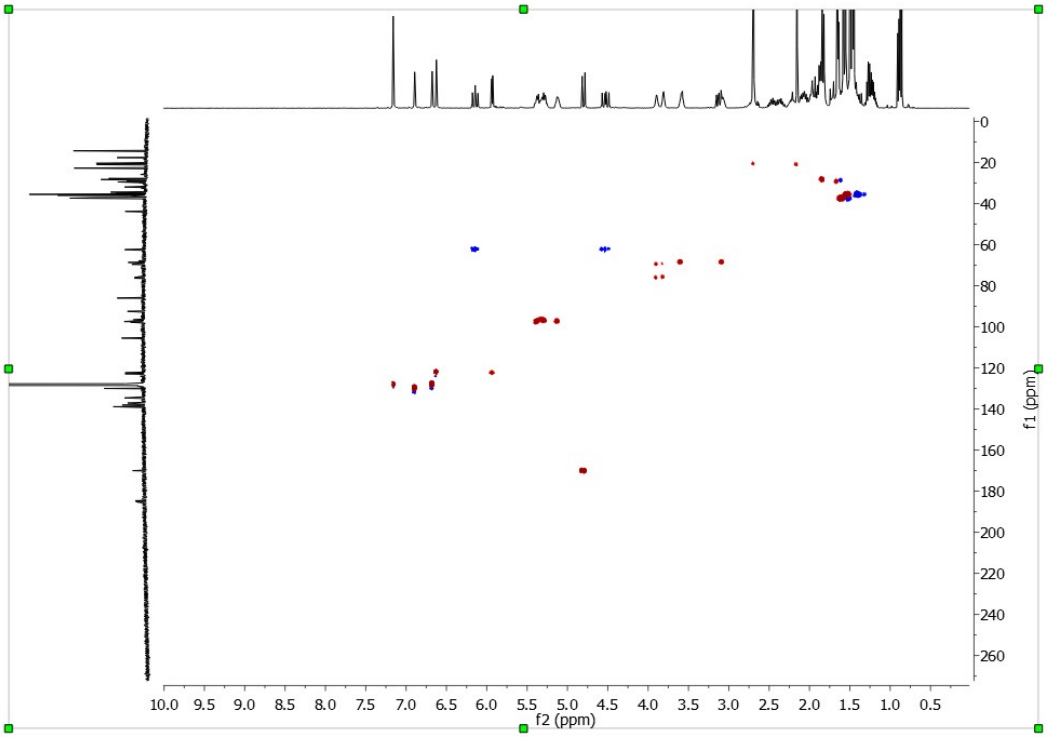


Figure S5. ^{1}H NMR spectrum of a 1:1 co-crystallized mixture of complexes **2** (pink dots) and **4** (green dots) (500 MHz, C_6D_6, 296 K).

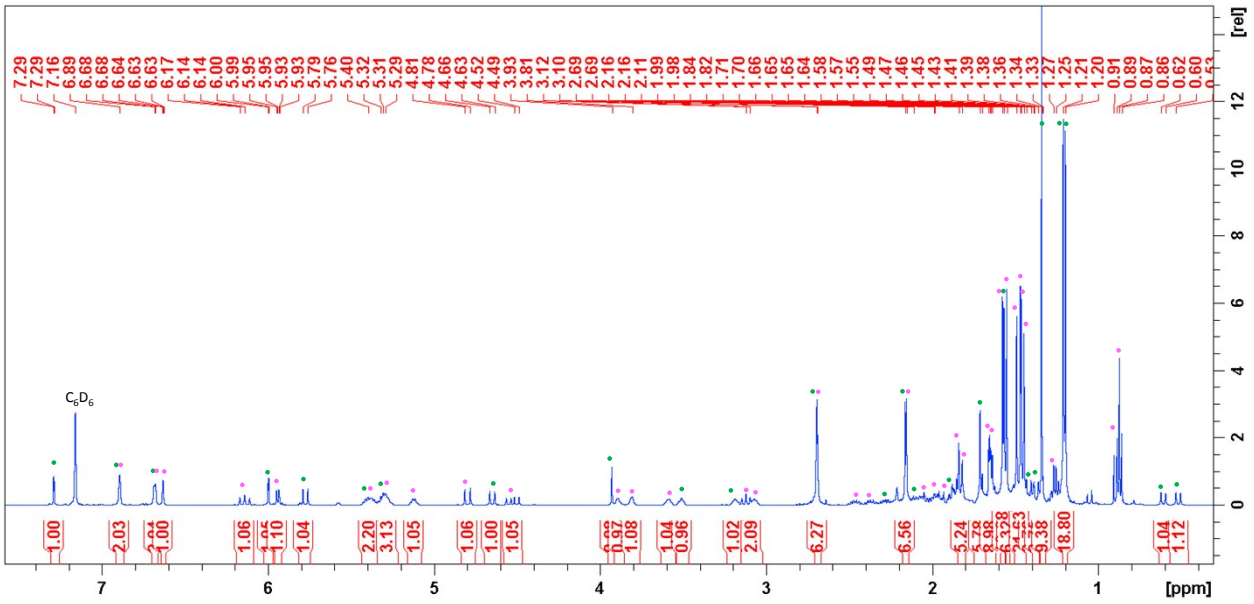


Figure S6. ^{1}H-^{13}C HSQC NMR spectrum of a 1:1 co-crystallized mixture of complexes **2** and **4** (500 MHz, C_6D_6, 296 K), showing notably a correlation between the ^{1}H singlet at δ = +3.93 ppm attributed to the Ta neopentyliene α-H and the characteristic neopentylidene ^{13}C resonance found at δ = +238.2 ppm.

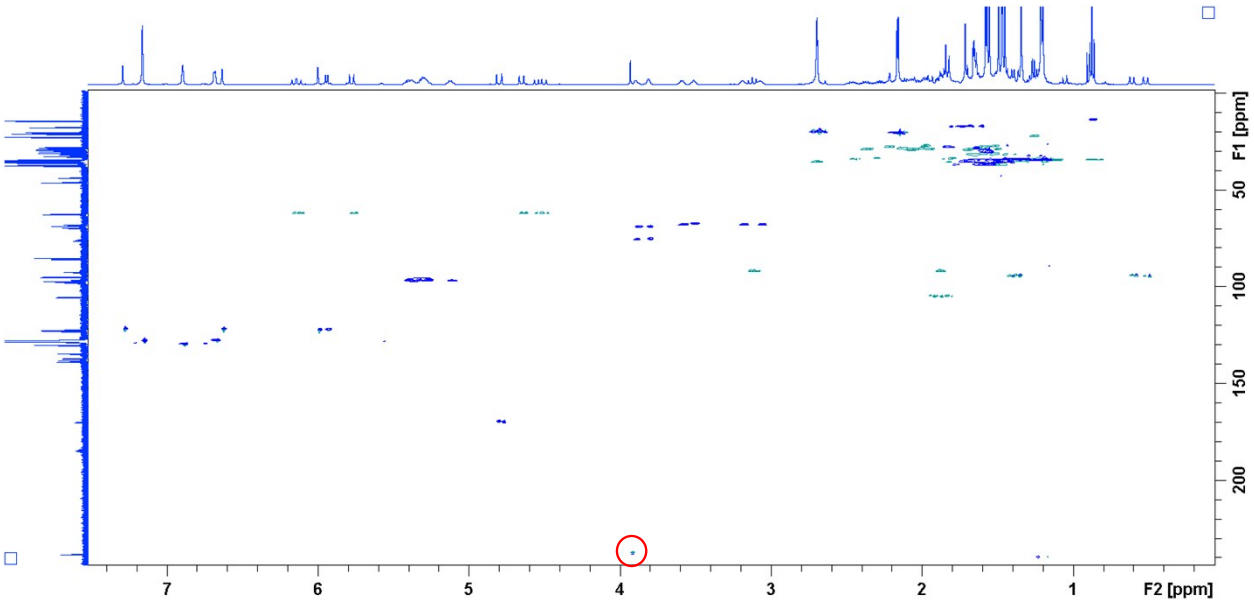


Figure S7. ^{1}H NMR spectrum of the complex **5** (400 MHz, C_6D_6, 296 K).

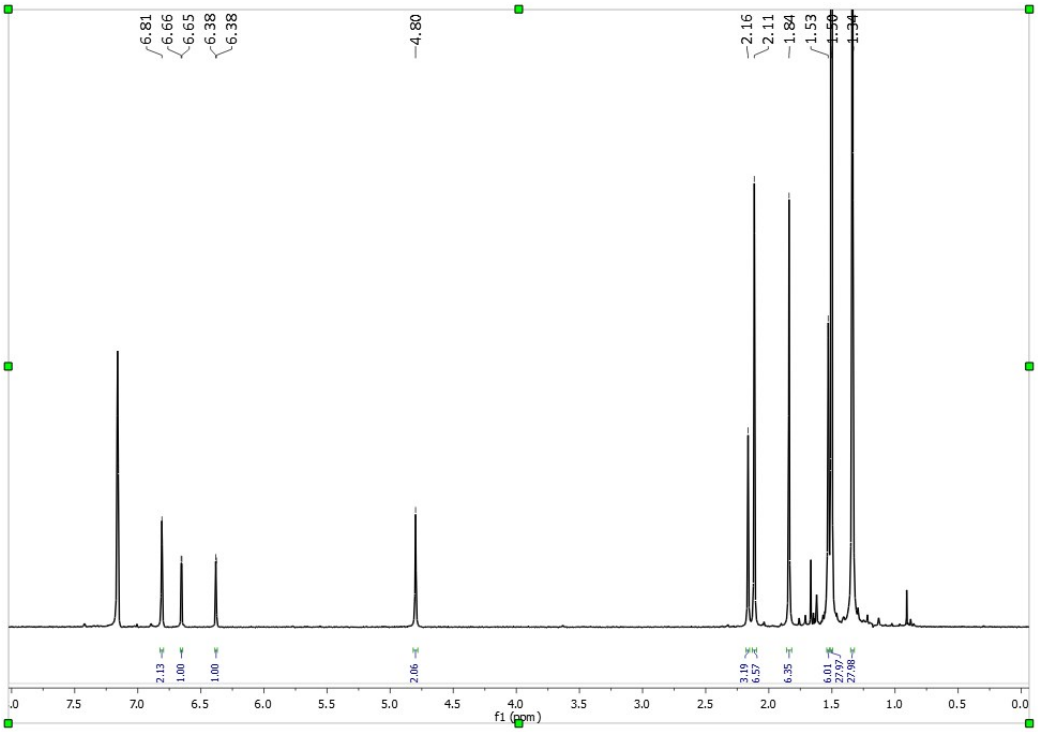


Figure S8. ^{13}C {^{1}H} NMR spectrum of the complex **5** (100 MHz, C_6D_6, 296 K).

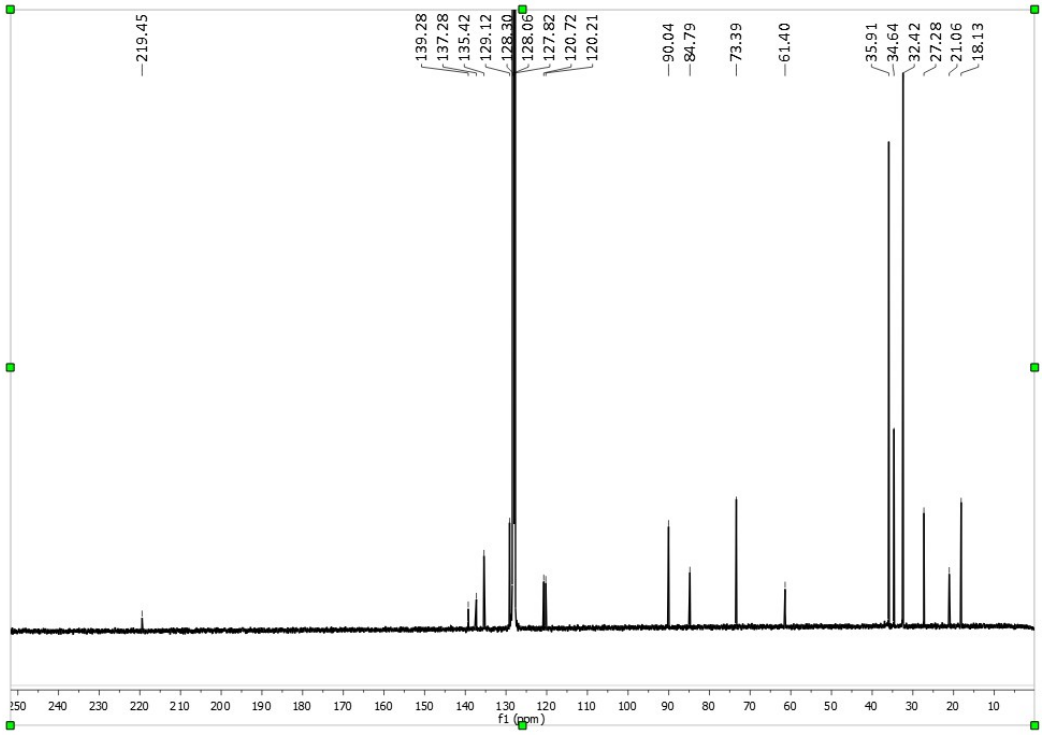


Figure S9. ^{1}H NMR spectrum of the complex **6** (400 MHz, C_6D_6, 296 K).

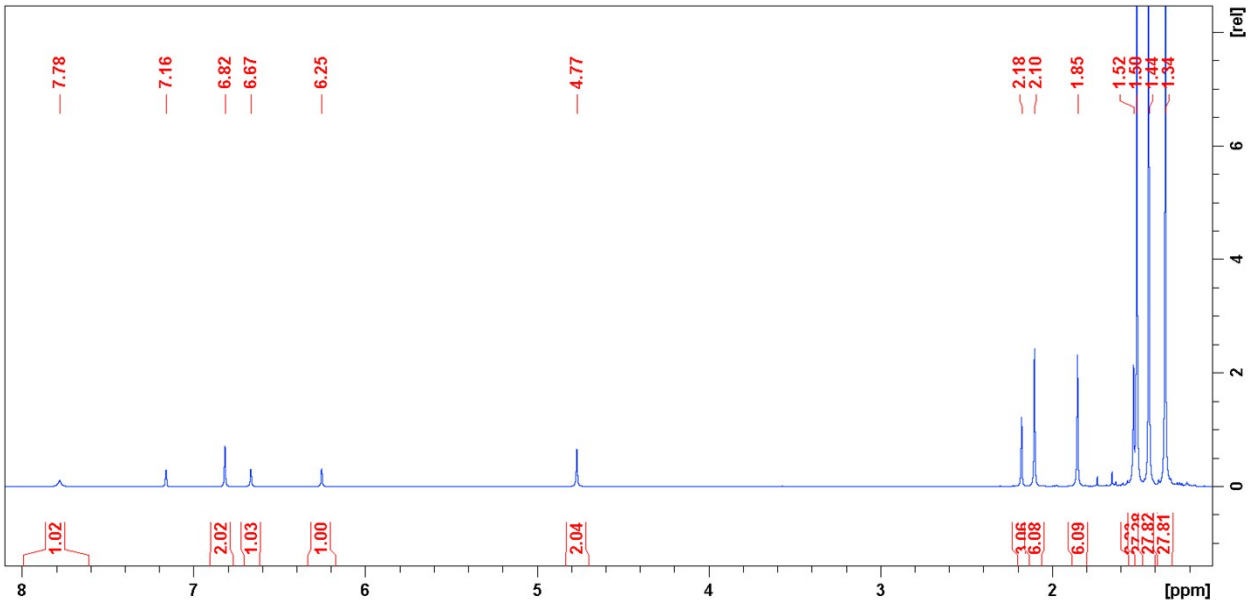


Figure S10. ^{13}C $\{^{1}H\}$ NMR spectrum of the complex **6** (100 MHz, C_6D_6, 296 K).

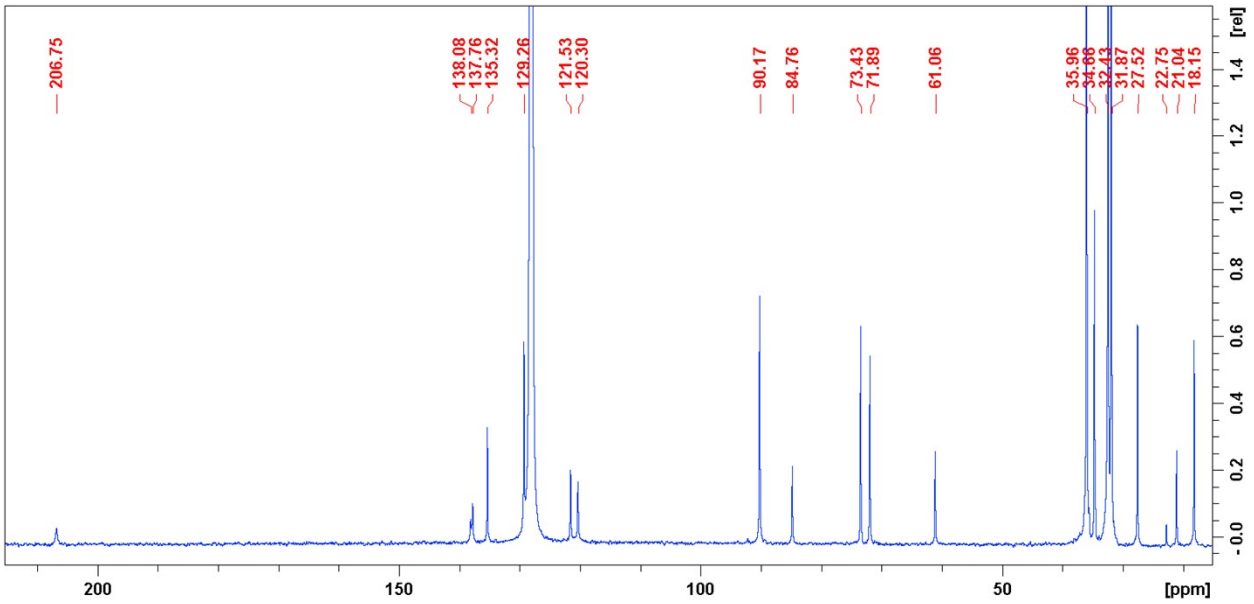


Figure S11. ^{1}H NMR spectrum (400 MHz, C_6D_6, 296 K) of complex **5** obtained from treatment of complex **6** at 120°C under vacuum in the solid-state.

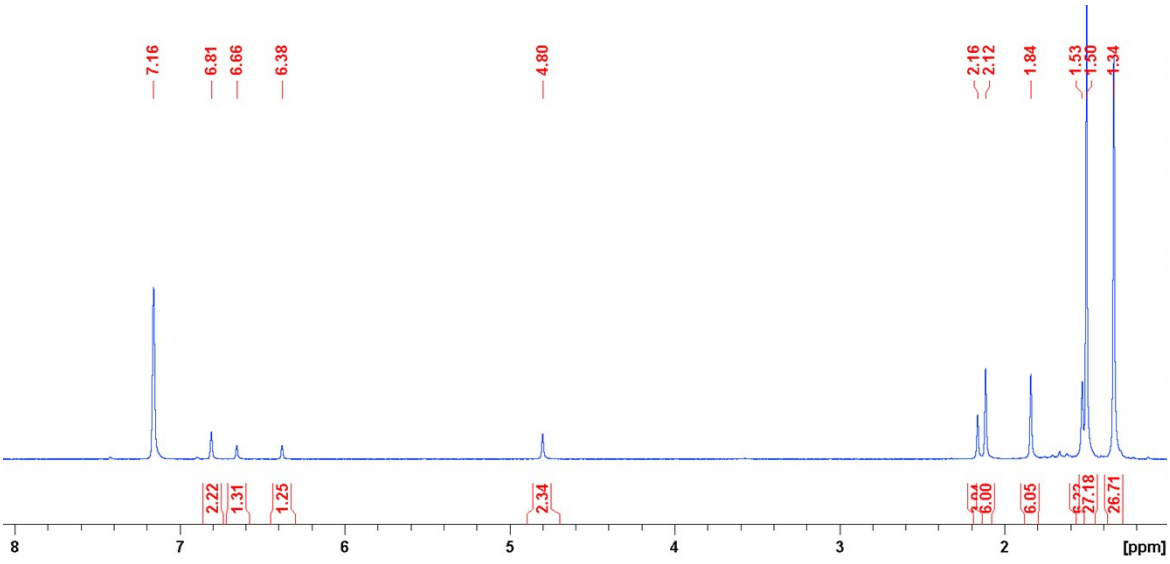


Figure S12. ^{1}H NMR spectrum of the complex **7** (500 MHz, THF-d_8, 296 K).

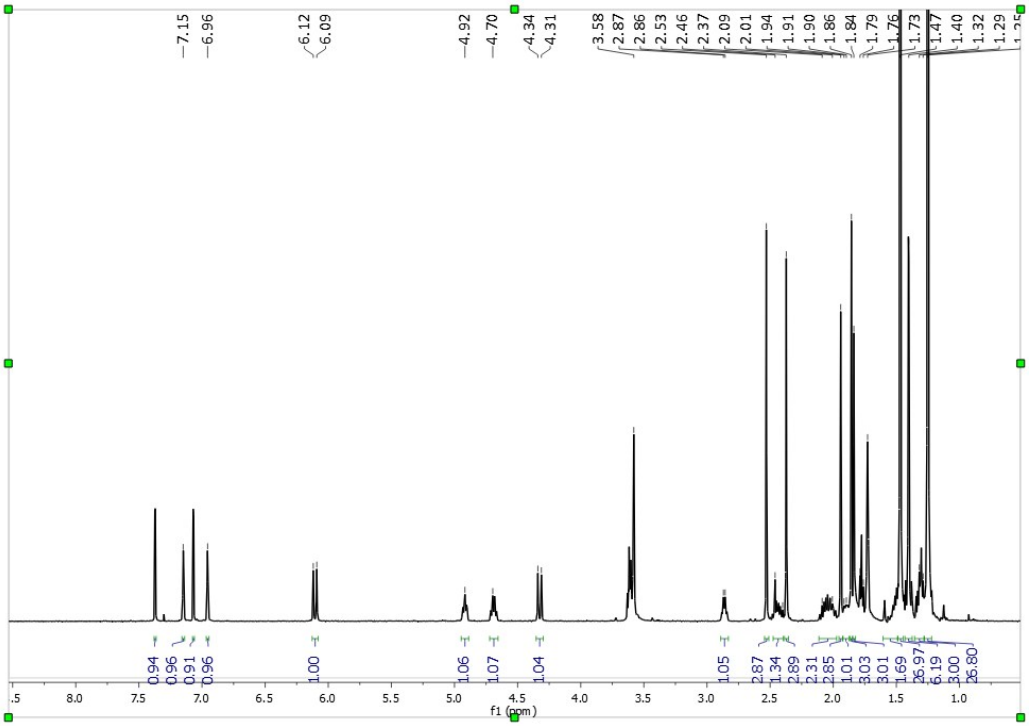
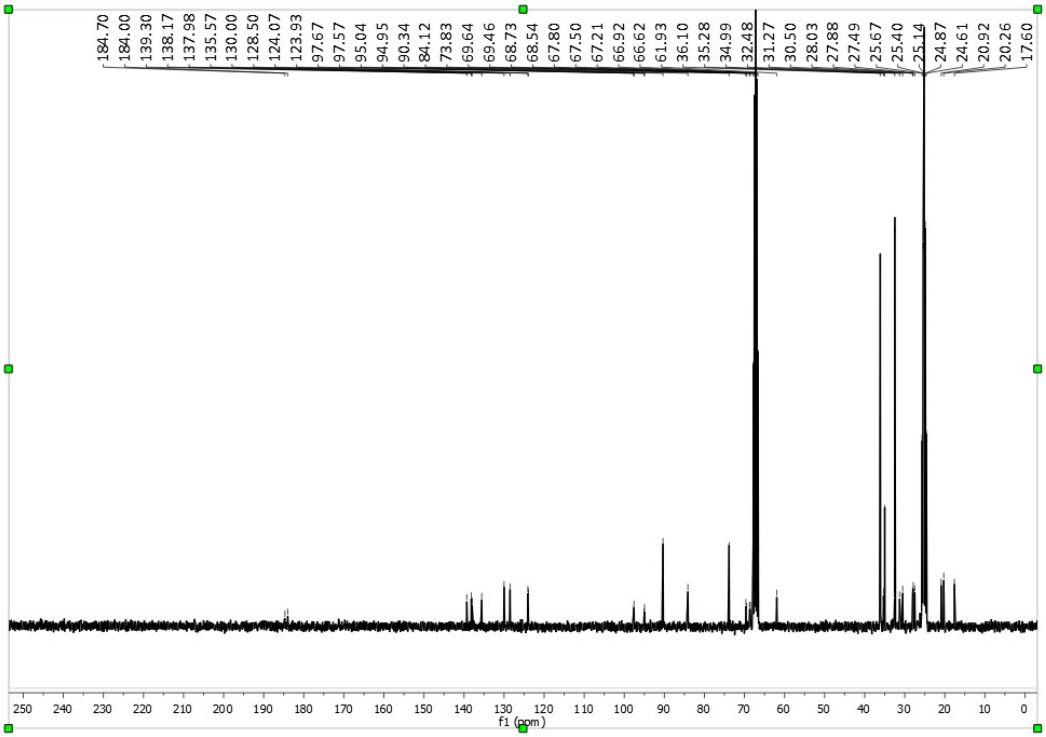


Figure S13. ^{13}C {^{1}H} NMR spectrum of the complex **7** (125 MHz, THF-d_8, 296 K).



B. IR spectroscopic data

Figure S14. DRIFT spectrum for trimetallic complex **2** (25°C, KBr solid solution under argon)

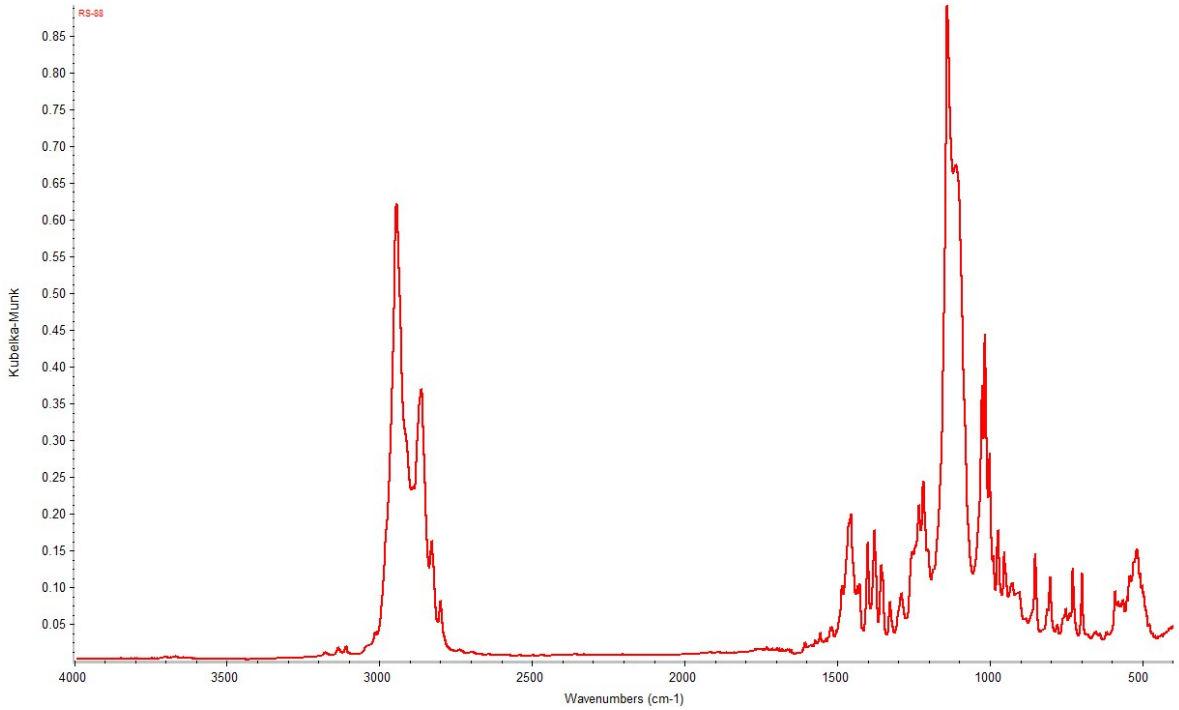


Figure S15. DRIFT spectrum for complex **5** (25°C, KBr solid solution under argon)

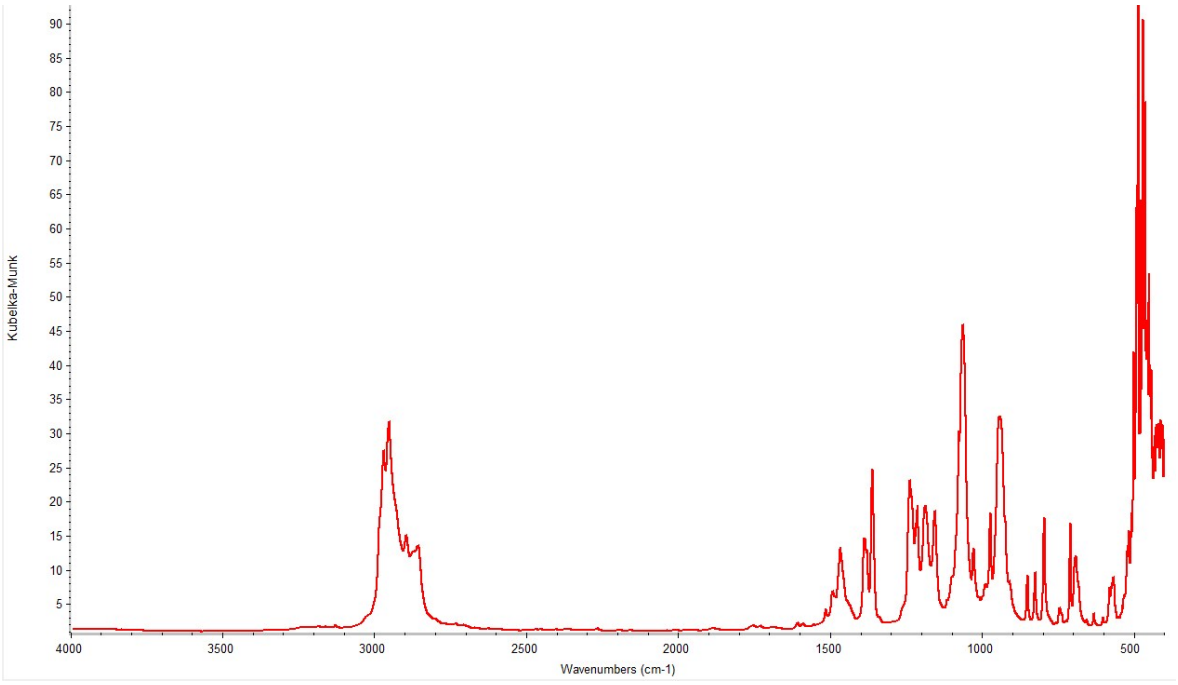


Figure S16. DRIFT spectrum for complex **6** (25°C, KBr solid solution under argon)

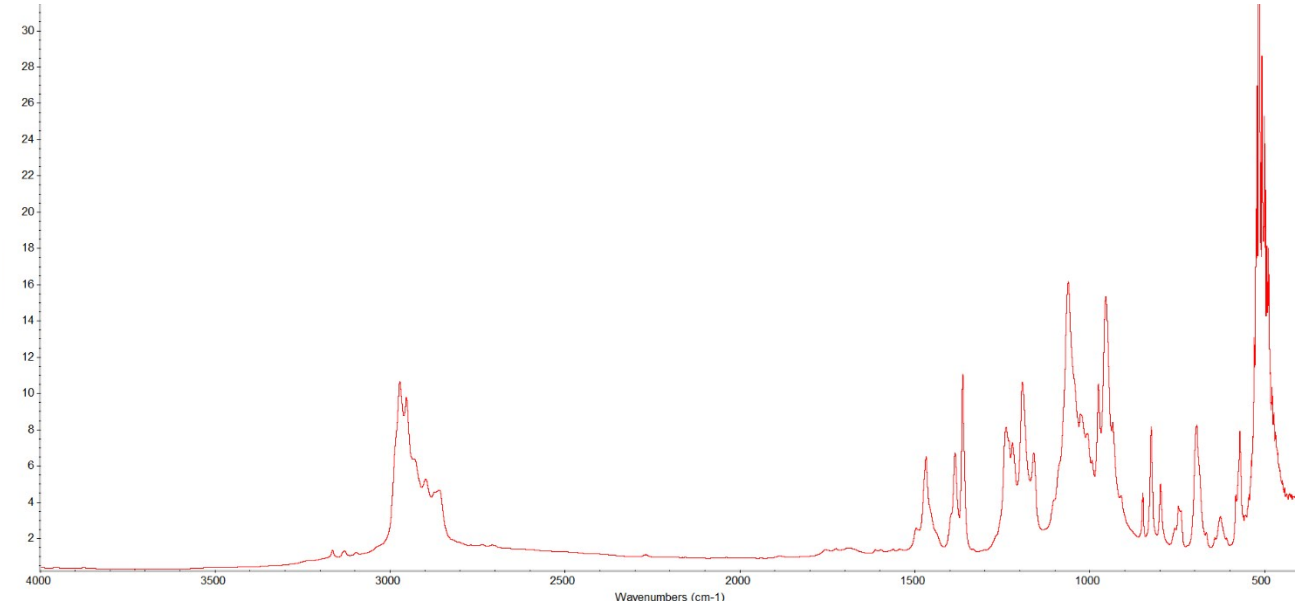
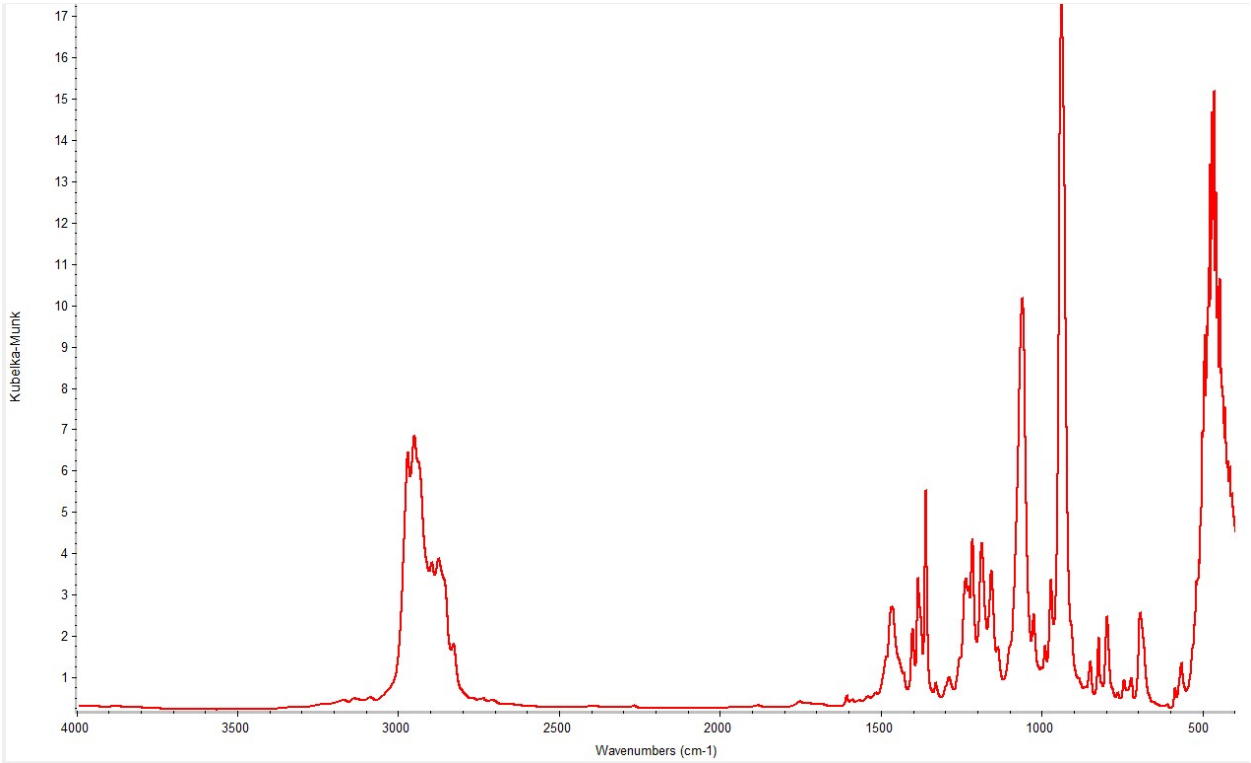
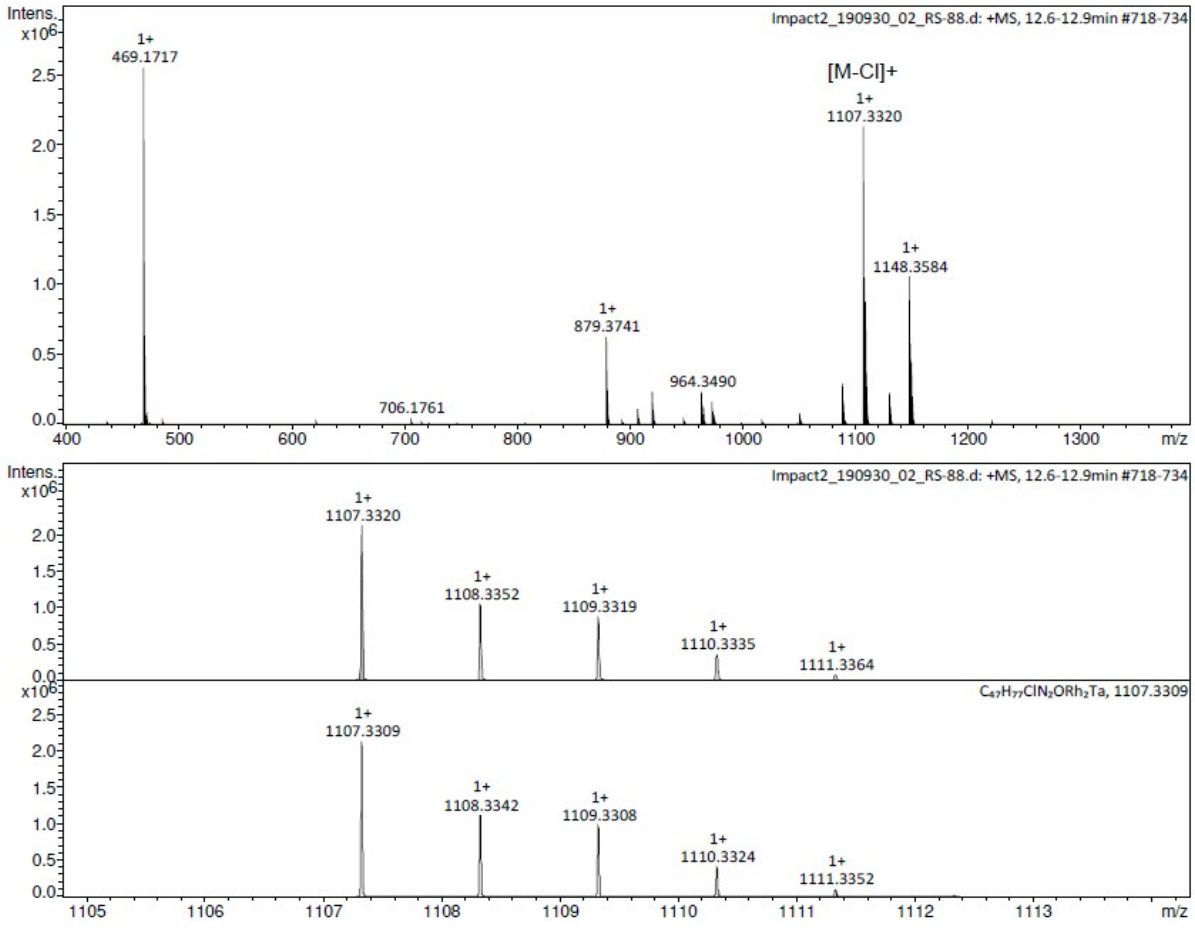


Figure S17. DRIFT spectrum for complex **7** (25°C, KBr solid solution under argon)



C. HRMS-ESI data

Figure S18. HRMS-ESI spectrum of the trimetallic complex **2**.



Meas. m/z	Ion Formula	m/z	err [ppm]	mSigma
1107.3320	C47H77ClN2ORh2Ta	1107.3309	-1.0	27.6

D. X-ray crystallography

X-ray structural determinations were performed at the centre de diffractométrie Henri Longchambon, Université de Lyon. A suitable crystal coated in Parabar-10312 oil was selected and mounted on a Gemini kappa-geometry diffractometer (Agilent Technologies UK Ltd) equipped with an Atlas CCD detector and using Mo radiation (λ= 0.71073 Å). Intensities were collected at 150 or 100 K by means of the CrysalisPro software. Reflection indexing, unit-cell parameters refinement, Lorentz-polarization correction, peak integration and background determination were carried out with the CrysalisPro software. An analytical absorption correction was applied using the modeled faces of the crystal.[1] The resulting set of hkl was used for structure solution and refinement. The structures were solved by direct methods with SIR97[2] and the least-square refinement on F2 was achieved with the CRYSTALS software.[3] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were all located in a difference map, and then were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C---H in the range 0.93--0.98 Å) and Uiso(H) (in the range 1.2-1.5 times Ueq of the parent atom), after which the positions were refined with riding constraints.

Table S1. Crystallographic parameters for compounds **3**, **4**, **6** and **7**.

Compound	**3**	**4**	**6**	**7**
Formula	$C_{26}H_{41}N_2O_1Ta_1$	$C_{39}H_{65}Cl_1N_2O_1Rh_1Ta_1$	$C_{55}H_{109}N_2O_9Si_2Ta_1$	$C_{51}H_{93}Cl_1N_2O_5Rh_1Si_1Ta_1$
cryst syst	triclinic	monoclinic	triclinic	triclinic
space group	*P*-1	$P2_1/n$	*P*-1	*P*-1
volume (Å^3)	1297.24(18)	4129.9(5)	3381.4(2)	3110.1(3)
a (Å)	8.6557(7)	10.0011(7)	9.7495(4)	14.7519(8)
b (Å)	10.8781(7)	15.523(1)	16.7483(7)	15.0383(9)
c (Å)	15.8244(1)	26.6754(19)	21.3697(8)	15.8880(8)
α (deg)	71.346(6)	90	95.525(3)	68.473(5)
β (deg)	75.611(7)	94.253(6)	102.339(3)	71.745(5)
γ (deg)	68.301(7)	90	93.414(3)	85.878(5)
Z	2	4	2	2
formula weight (g/mol)	578.57	897.24	1181.58	1161.70
density (g cm^{-3})	1.48	1.443	1.160	1.240
absorption coefficient (mm^{-1})	4.255	3.141	1.707	2.124
temp (K)	150.0(1)	150.0(1)	100.0(1)	150.0(1)
total no. reflections	30768	56886	90751	70217
unique reflections [R(int)]	6555 [0.068]	10862 [0.097]	17805 [0.0638]	15794 [0.060]
Final R indices [I > 2σ(I)]	R1 = 0.0433 wR2 = 0.1234	R1 = 0.0702 wR2 = 0.1813	R1 = 0.0473 wR2 = 0.1027	R1 = 0.0629 wR2 = 0.1301
GoF	0.9970	1.0076	1.090	0.9557

E. Detailed characterization of complex 6

The addition of two equivalents of $HOSi(O^tBu)_3$ onto **1**, carried out either in pentane or toluene, yields the silanol-NHC adduct, $\{HOSiO^tBu_3\}\{Ta(L)[OSi(O^tBu)_3](CH_2{}^tBu)_3\}$, **6**. The ^1H NMR spectrum for **6** exhibits a highly shifted singlet resonance for the hydroxyl proton at δ = 7.78 ppm. The ^{13}C NMR spectrum for **6** is particularly diagnostic. The ^{13}C carbene resonance is shifted upfield in comparison with that for **5** (δ = +206.8 versus +219.4 ppm respectively), which indicates that the carbene is engaged into electronic donation to the hydroxyl proton. Similar behaviour was previously reported by our group for the free hydroxyl-carbene 1-mesityl-3-(2-hydroxyisobutyl)imidazol-2-ylidene ligand[4] and also for *N,N'*-bis(mesityl)imidazol-2-ylidene (IMes) in the presence of methanol, whose ^{13}C carbenic resonance is shifted from δ = 219.7 ppm[5] in the absence of methanol to δ = 203.9 ppm[6] in the IMes-methanol H-bonded adduct. The solid-state structure of **6**, which is reproduced below on Figure S18, is a rare example of a silanol-carbene hydrogen-bonded adduct. The measured distance between the hydroxyl oxygen and the NHC carbon is short (2.782(5) Å) and is consistent with hydrogen bonding. The silanol-carbene formulation proposed for **6** is confirmed by the values of the C1-N_{imid} bond lengths (1.357(5) and 1.358(5) Å) and the N1-C1-N2 ring angle (102.9(3)°) (typical range for NHCs: 1.35-1.37 Å and 101-105°).[4,7–10] In the symmetrically opposite siloxy-imidazolium situation, a shortening of the C-N_{imid} bond lengths and a relaxation of the NCN ring angle would have been expected (typical range for imidazoliums: 1.31-1.34 Å and 107-110°).[4,7–10]

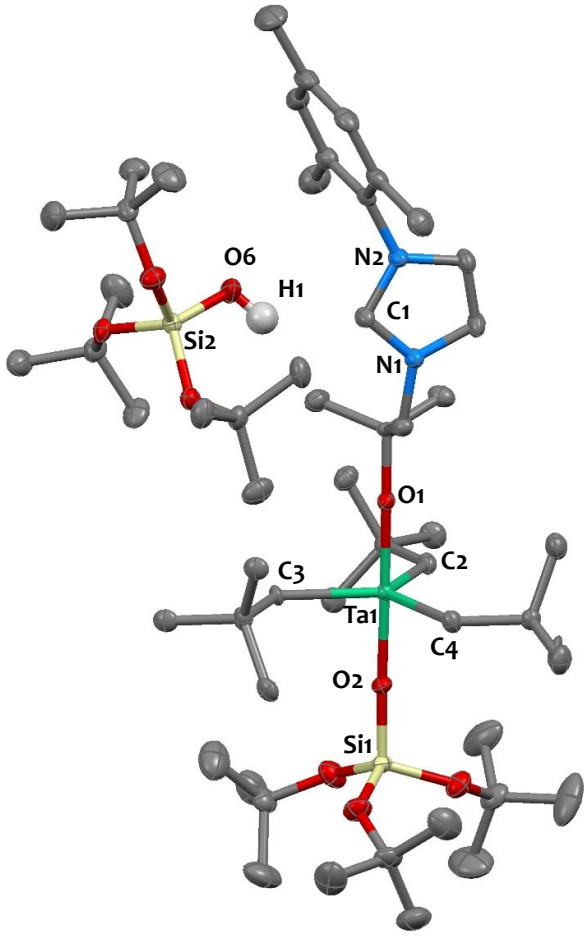


Figure S19. Solid-state molecular structure of **6** (50% probability ellipsoids). Hydrogen atoms, except that of the silanol group (H1) have been omitted for clarity. Selected bond distances (Å) and angles (°): Ta1-O1 1.883(3); Ta1-O2 1.921(3); Ta1-C2 2.162(4); Ta1-C3 2.150(3); Ta1-C4 2.165(4); O6···C1 2.782(5); N1-C1 1.357(5); N2-C1 1.358(5); O1-Ta1-O2 179.0(1); N1-C1-N2 102.9(3); O6-H1···C1 137.8(3).

F. References

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