

Supporting Information for :

Zr vs. Ti Molecular and Silica-Supported Imido Complexes in Stoichiometric and Catalytic Oxo/Imido Heterometathesis

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NMR Spectra of Molecular Complexes

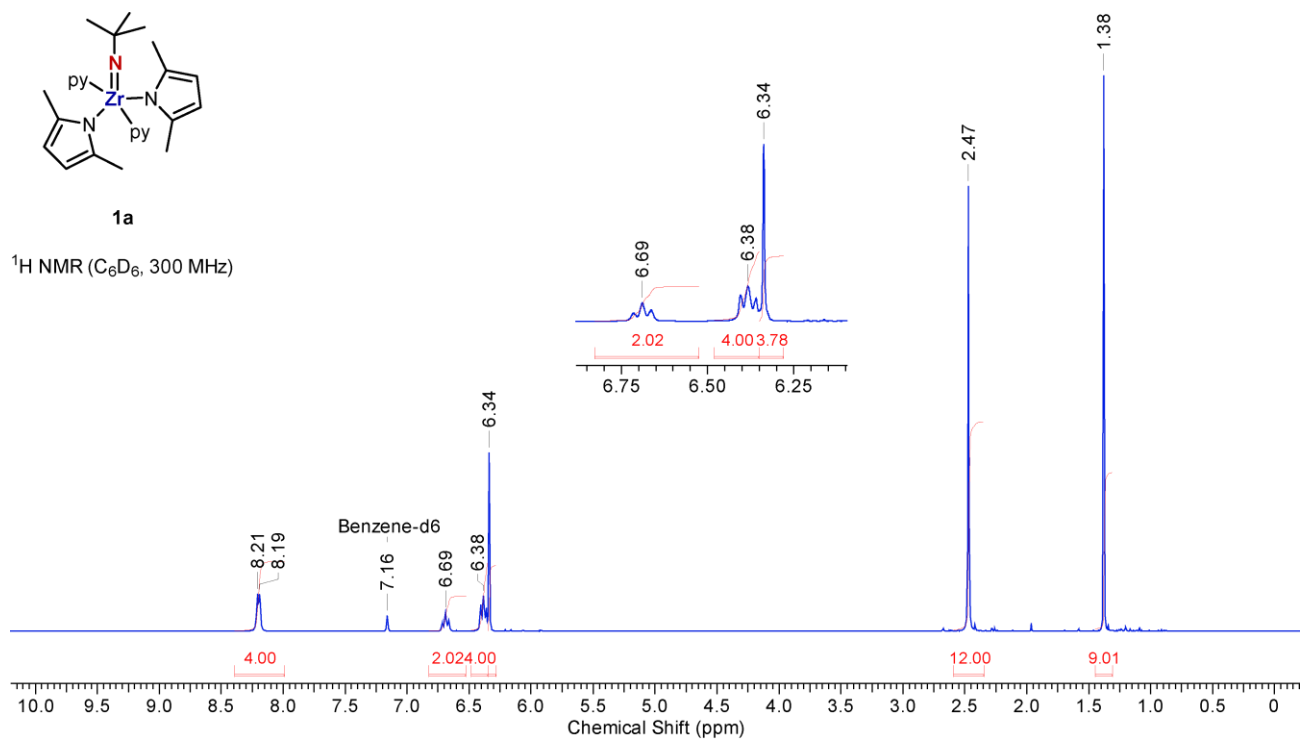


Fig. S1. $^1\text{H NMR}$ spectrum of $\text{Zr}(=\text{NtBu})(\text{Me}_2\text{Pyr})_2(\text{py})_2$ (**1a**).

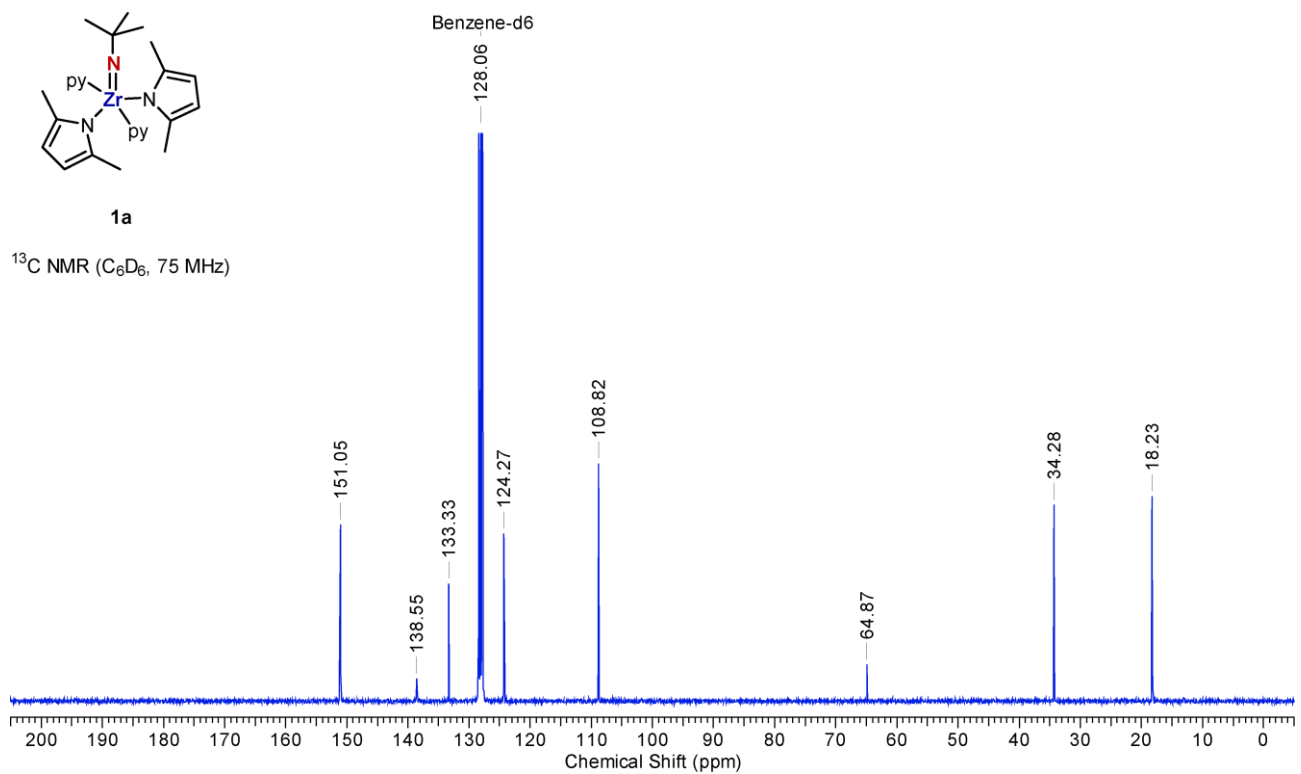
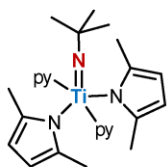


Fig. S2. $^{13}\text{C NMR}$ spectrum of $\text{Zr}(=\text{NtBu})(\text{Me}_2\text{Pyr})_2(\text{py})_2$ (**1a**).



2a

$^1\text{H NMR}$ (C_6D_6 , 200 MHz)

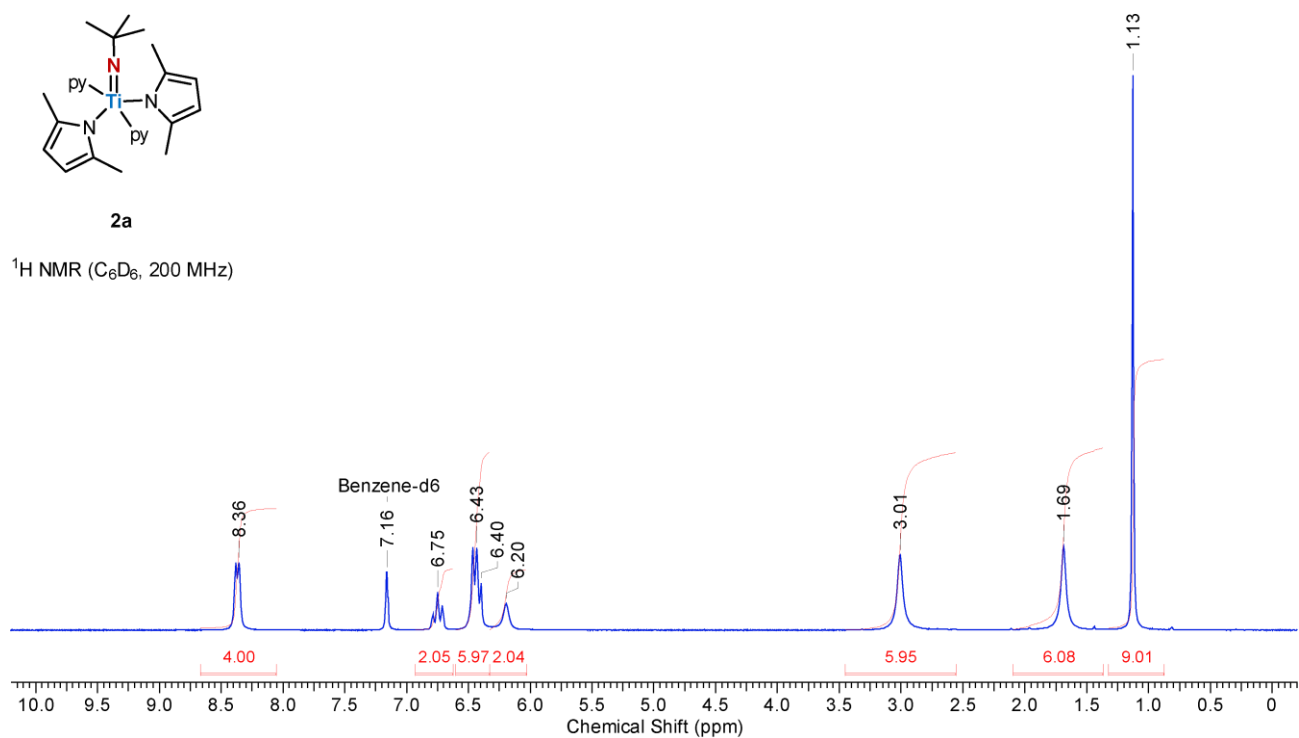
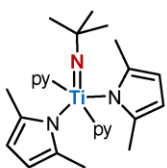


Fig. S3. $^1\text{H NMR}$ spectrum of $\text{Ti}(=\text{NtBu})(\text{Me}_2\text{Pyr})_2(\text{py})_2$ (**2a**).^[1]



2a

$^{13}\text{C NMR}$ (C_6D_6 , 75 MHz)

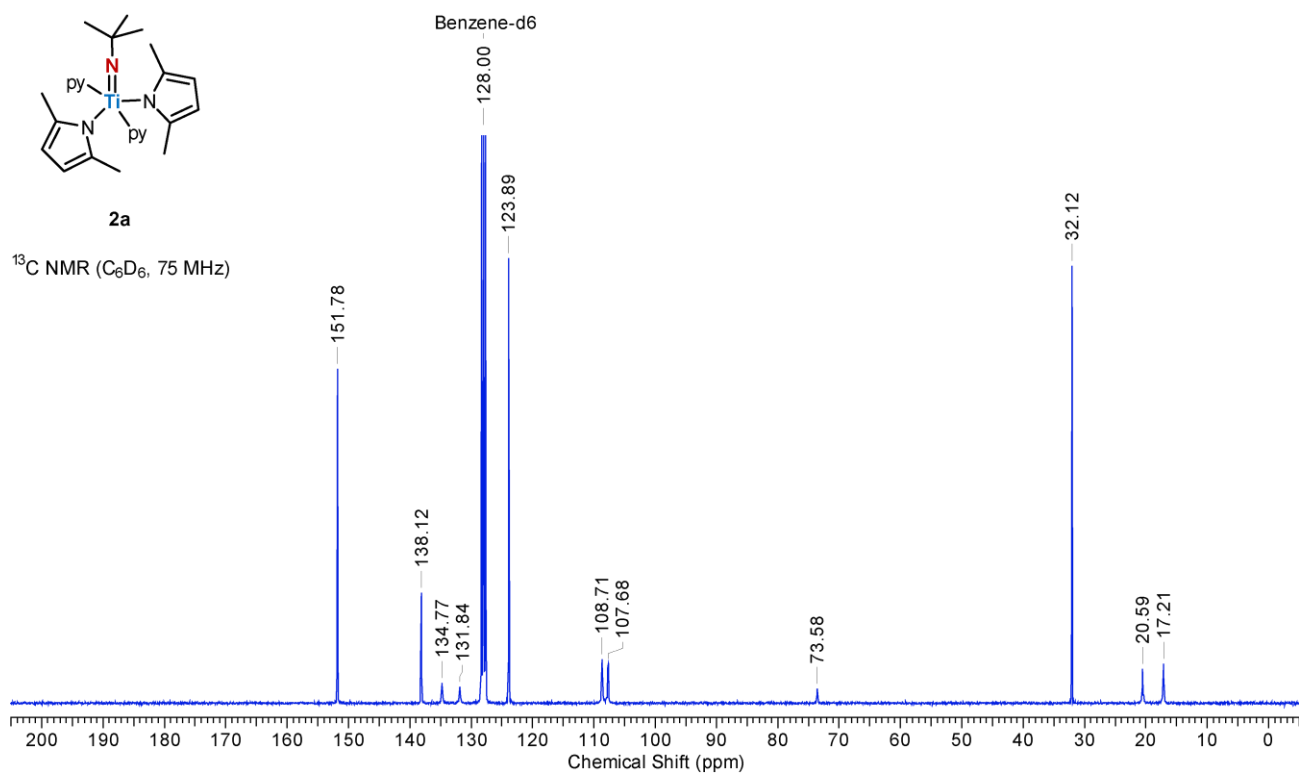


Fig. S4. $^{13}\text{C NMR}$ spectrum of $\text{Ti}(=\text{NtBu})(\text{Me}_2\text{Pyr})_2(\text{py})_2$ (**2a**).^[1]

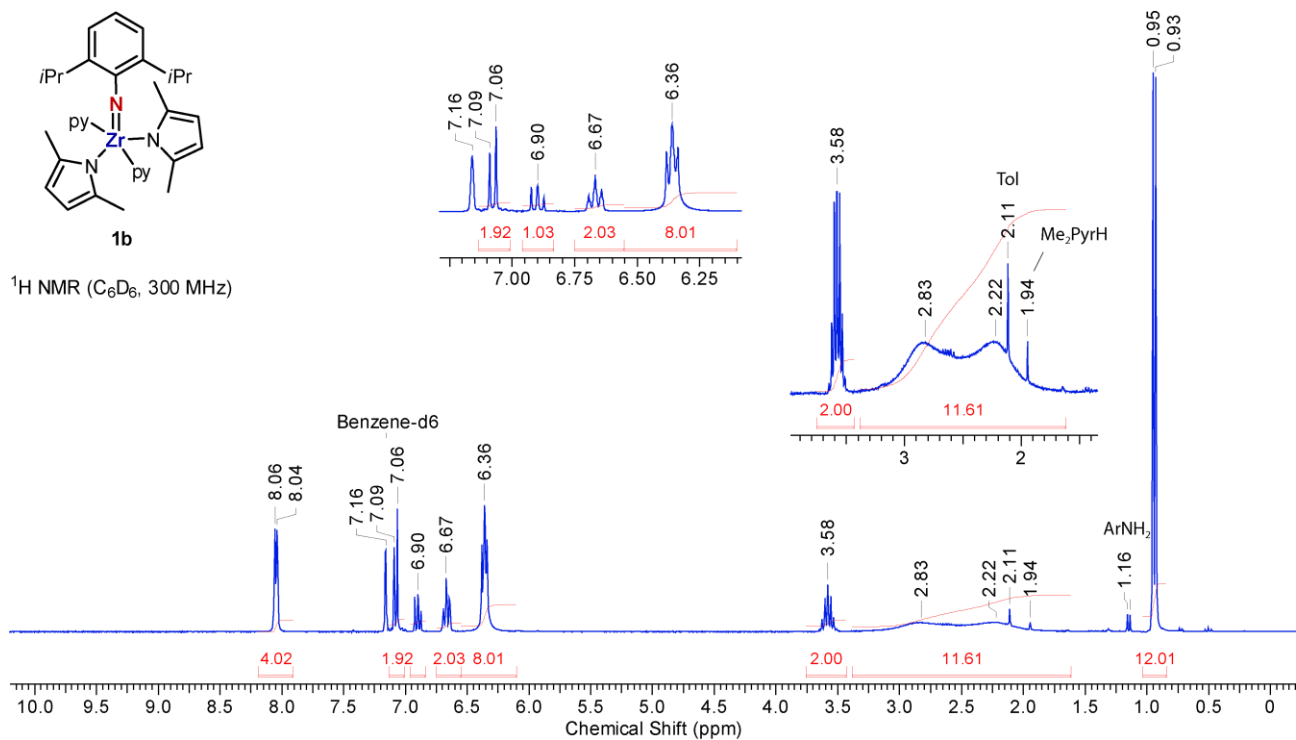


Fig. S5. $^1\text{H NMR}$ spectrum of $\text{Zr}(=\text{NAr})(\text{Me}_2\text{Pyr})_2(\text{py})_2$ (**1b**).

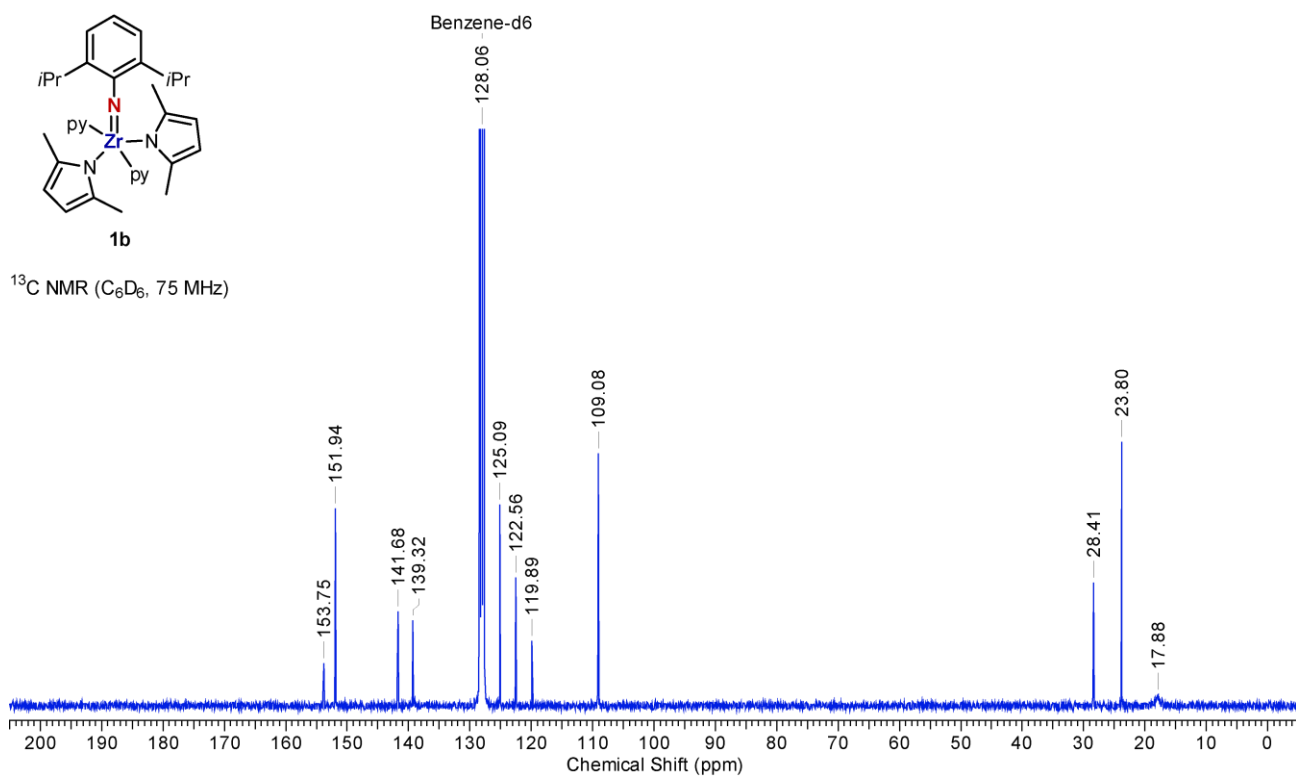


Fig. S6. $^{13}\text{C NMR}$ spectrum of $\text{Zr}(=\text{NAr})(\text{Me}_2\text{Pyr})_2(\text{py})_2$ (**1b**).

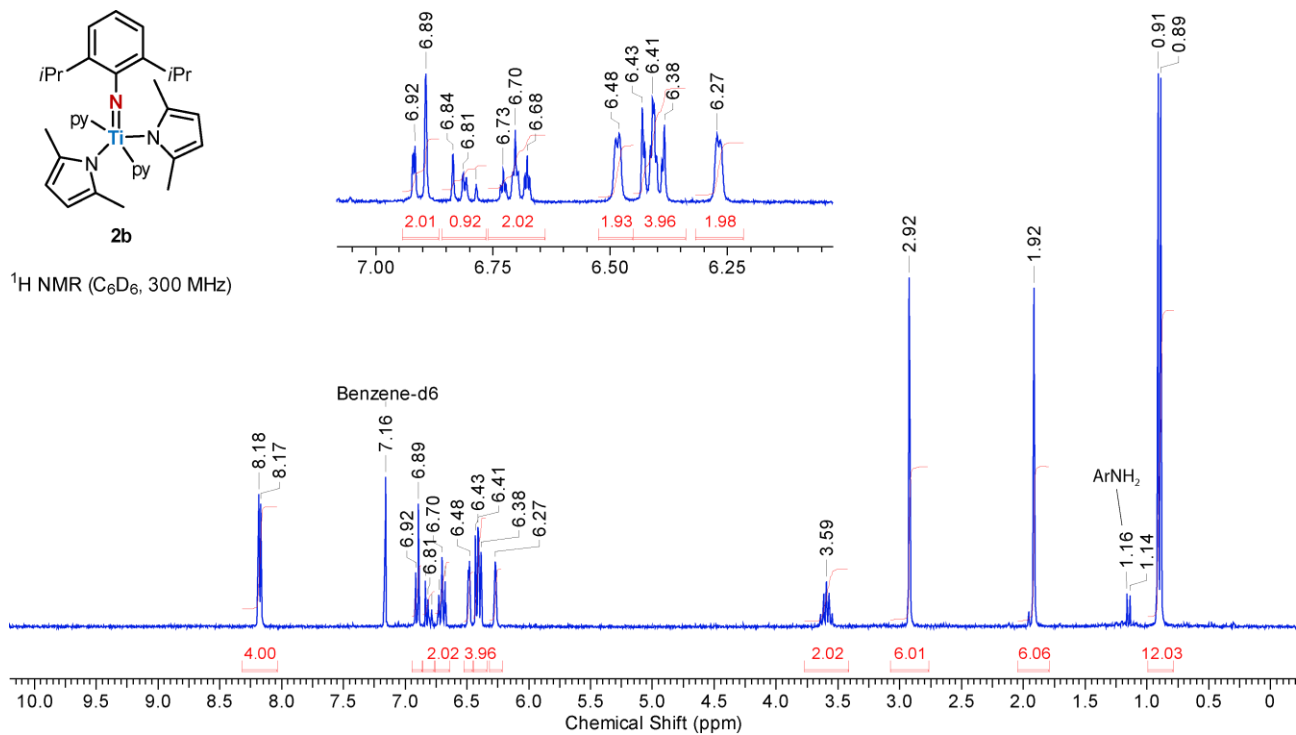


Fig. S7. ¹H NMR spectrum of Ti(=NAr)(Me₂Pyr)₂(py)₂ (**2b**).

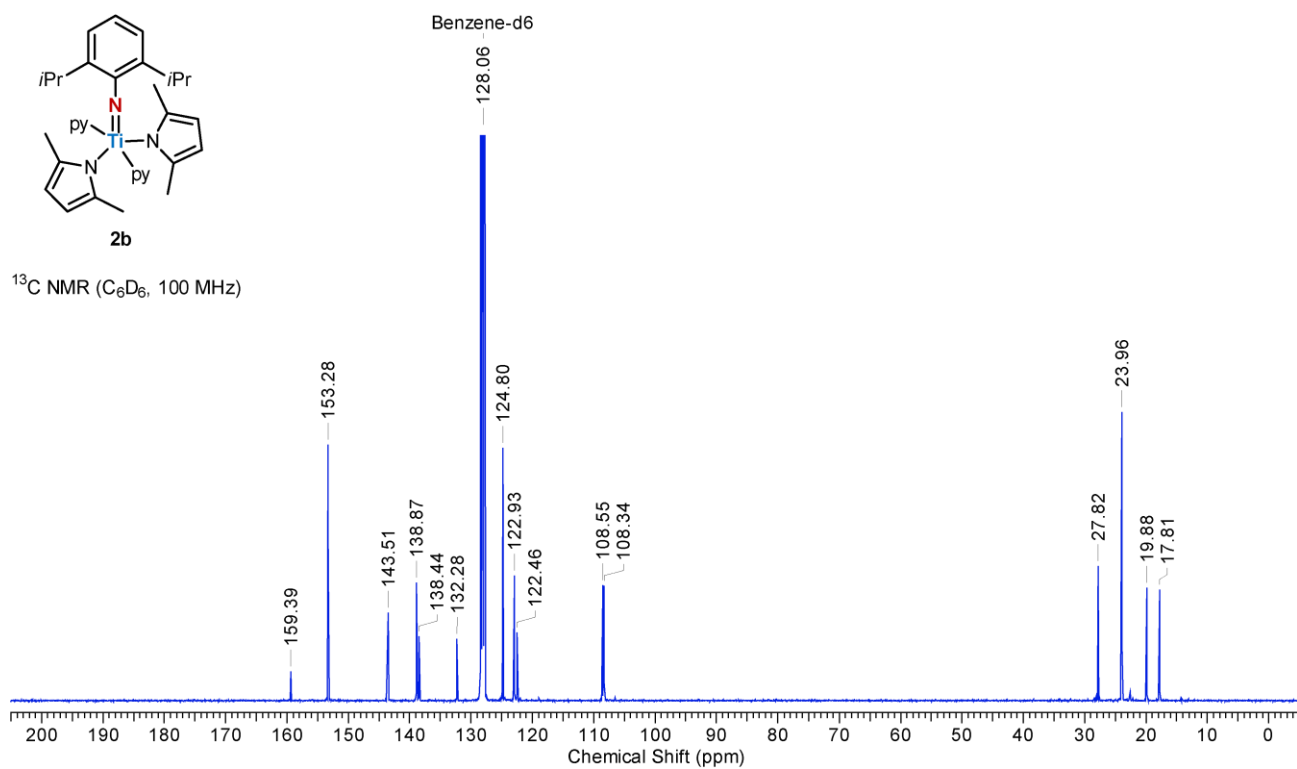


Fig. S8. ¹³C NMR spectrum of Ti(=NAr)(Me₂Pyr)₂(py)₂ (**2b**).

Solid-State NMR Spectra of Grafted Zr Complexes

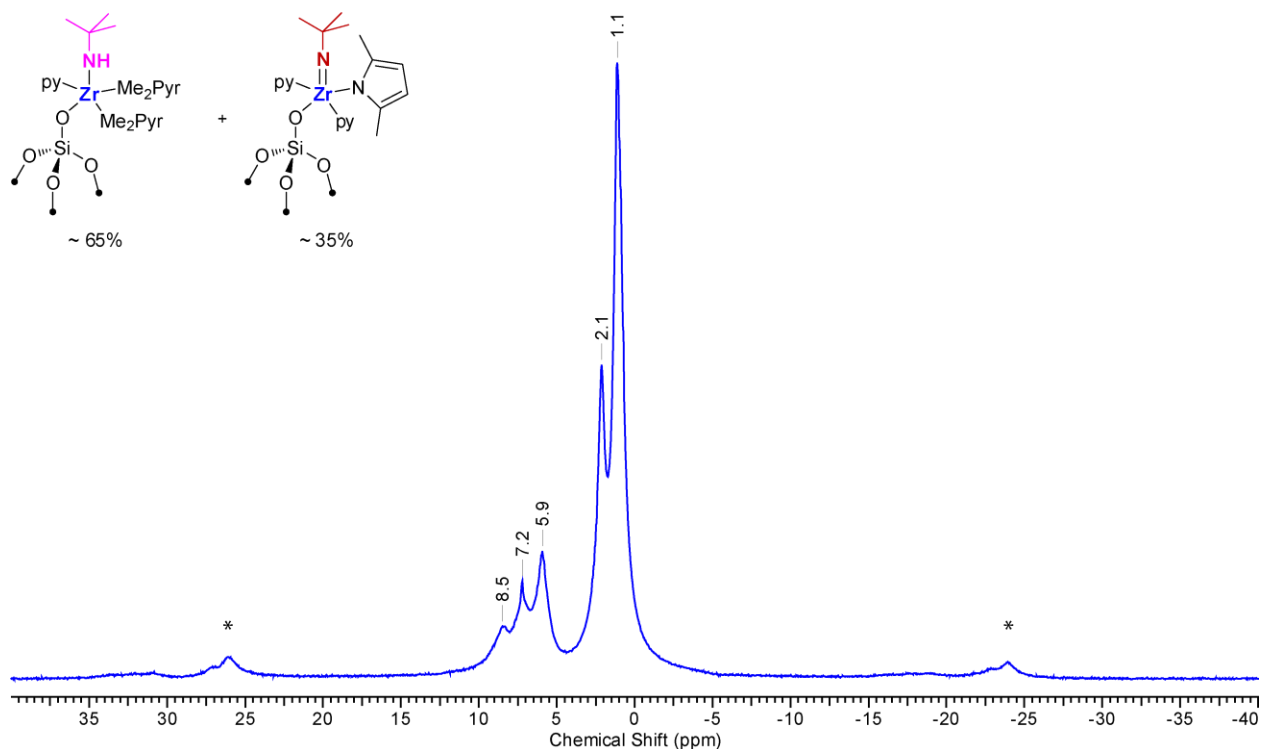


Fig. S9. ¹H MAS solid-state NMR spectrum of the material Zr(=NtBu)(Me₂Pyr)₂(py)₂/SiO₂₋₇₀₀ (**1a**/SiO₂) (400 MHz; 10 kHz MAS). Asterisks indicate spinning side-bands.

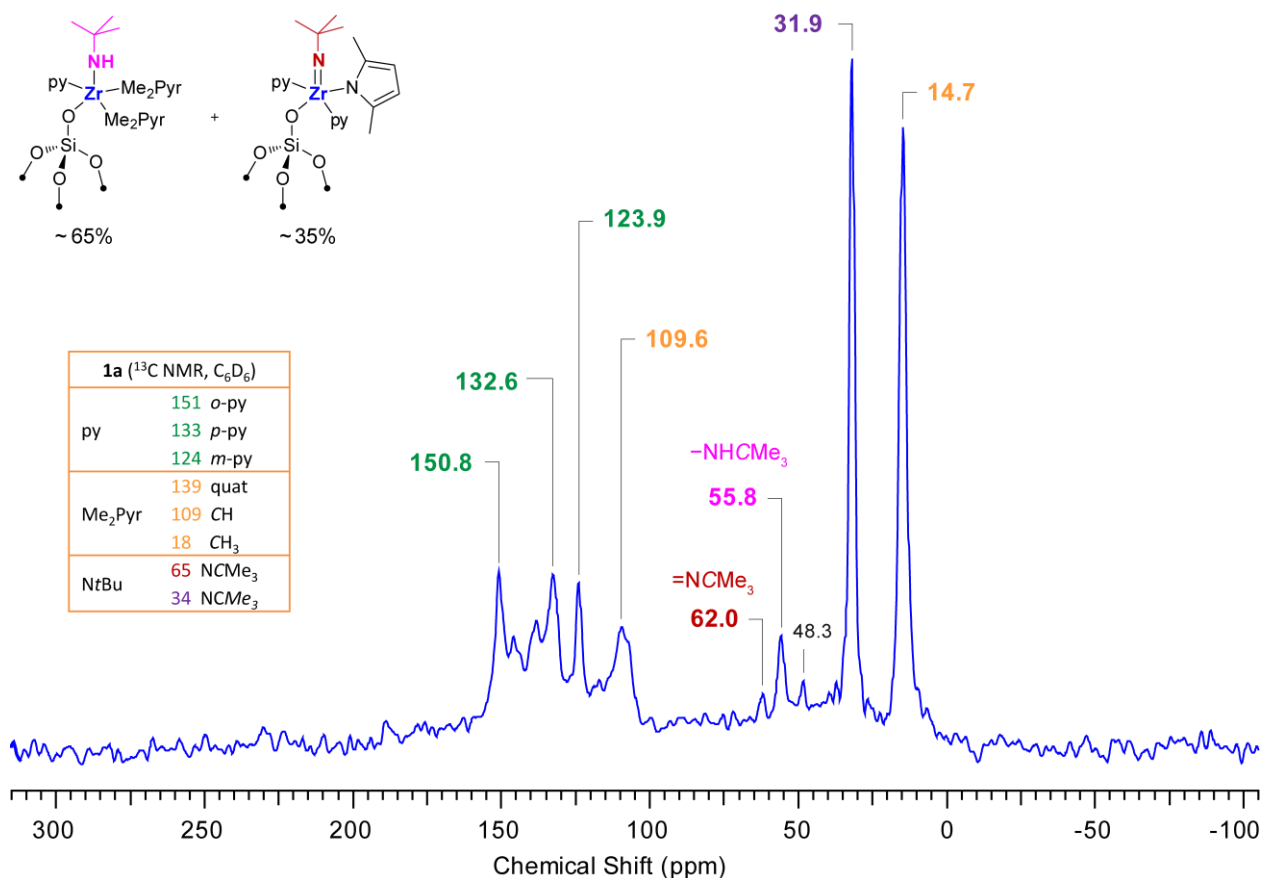


Fig. S10. ¹³C CP MAS solid-state NMR spectrum of the material Zr(=NtBu)(Me₂Pyr)₂(py)₂/SiO₂₋₇₀₀ (**1a**/SiO₂) (100 MHz; 10 kHz MAS; CP contact time 3 ms; recycle delay 2 s; 60'000 scans).

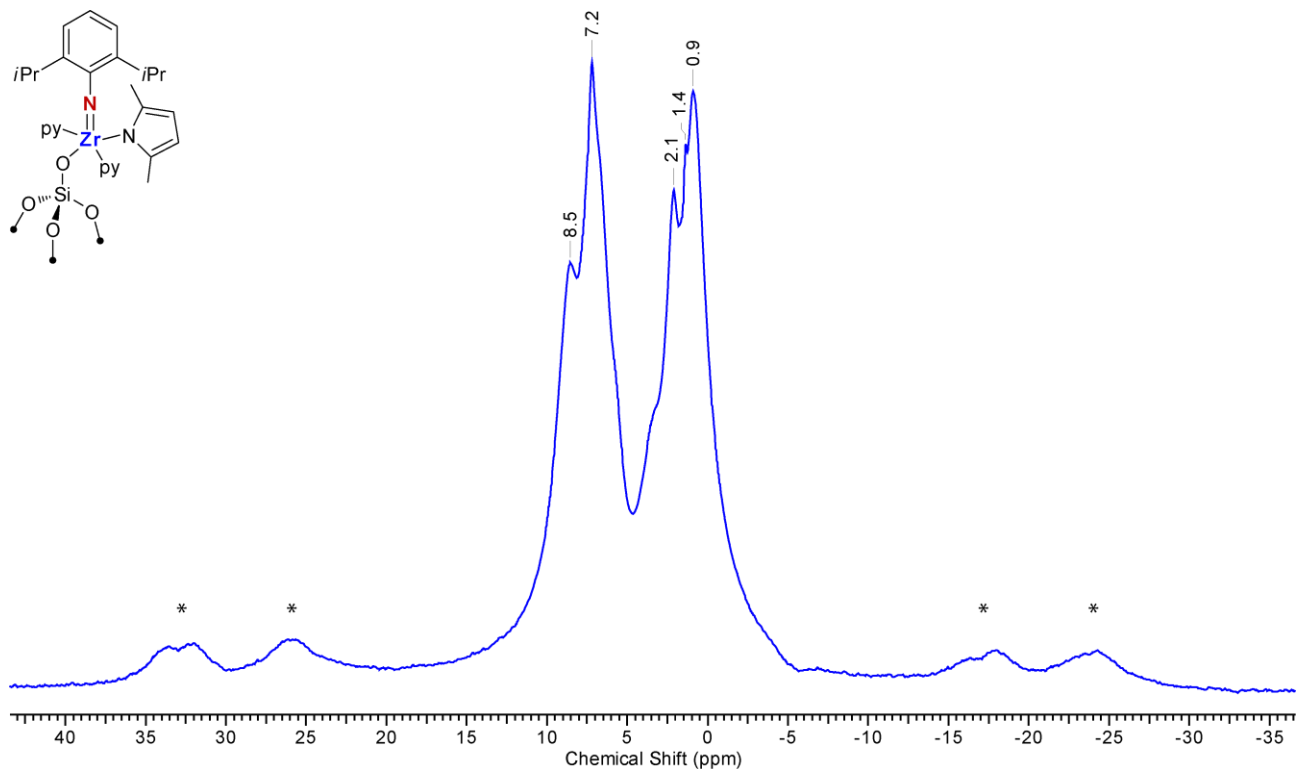


Fig. S11. ^1H MAS solid-state NMR spectrum of the material $\text{Zr}(=\text{NAr})(\text{Me}_2\text{Pyr})_2(\text{py})_2/\text{SiO}_{2-700}$ (**1b**/ SiO_2) (400 MHz; 10 kHz MAS). Asterisks indicate spinning side-bands.

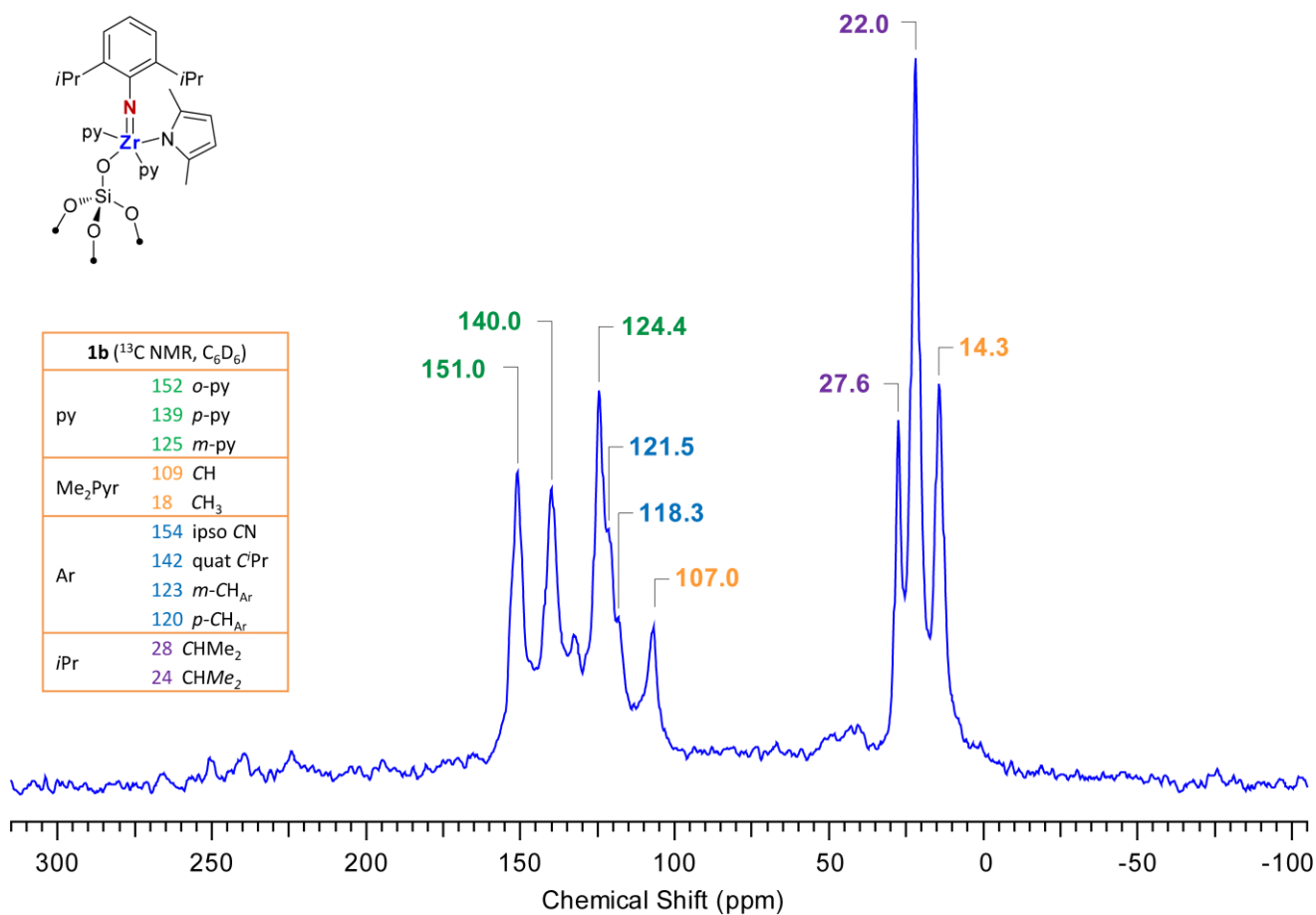


Fig. S12. ^{13}C CP MAS solid-state NMR spectrum of the material $\text{Zr}(=\text{NAr})(\text{Me}_2\text{Pyr})_2(\text{py})_2/\text{SiO}_{2-700}$ (**1b**/ SiO_2) (100 MHz; 10 kHz MAS; CP contact time 3 ms; recycle delay 2 s; 100'000 scans).

IR Spectra of Grafted Zr Complexes

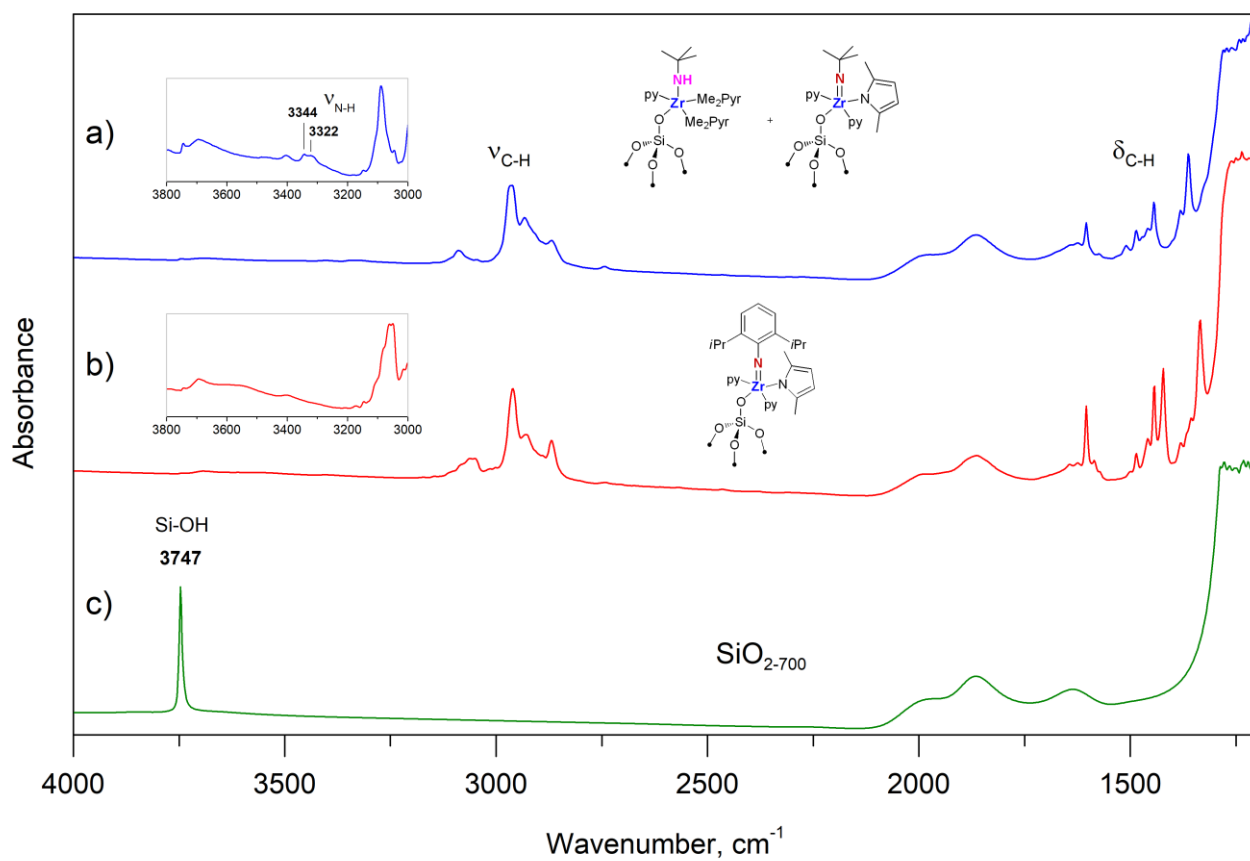


Fig. S13. IR spectra of the materials **1a/SiO₂** (a), **1b/SiO₂** (b), and **SiO₂₋₇₀₀** (c).

Stoichiometric Reactions of Molecular and Grafted Complexes

General procedure for the reactions with Ph₂CO. The pre-weighed amounts of complex, benzophenone and ferrocene (FCH) as an internal standard were placed in a J. Young NMR tube inside a glovebox, dissolved in Tol-d₈ or C₆D₆ and the reaction was monitored with ¹H NMR spectroscopy.

General procedure for the reactions of grafted complexes with Ph₂CO. The pre-weighed amounts of grafted material, benzophenone and FCH as an internal standard were placed in a J. Young NMR tube inside a glovebox, C₆D₆ was added and the liquid phase was monitored with ¹H NMR spectroscopy.

Quantification. In all experiments the absolute quantities n (μmols) of the compounds were calculated using the known amount of FCH ($n_i = n_{\text{FCH}} \times N_{\text{FCH}}/N_i \times A_i/A_{\text{FCH}}$, where A is a peak area and N is a number of protons corresponding to the peak, $N_{\text{FCH}} = 10$). The data is summarized in tables below together with representative spectra. For convenience of calculation FCH is integrated as 100 ($A_{\text{FCH}} = 100$) in all spectra. The vertical scale is kept constant for all figures within one experiment. All quantities in the tables are expressed in % relative to *the total initial amount of the metal complex* in the reaction because this allows one to directly estimate how much [NR] is transformed into the imine, how much extra benzophenone is consumed per 1 equiv of complex, etc. (the reaction loadings are given with every experiment so the quantities in μmols can be easily recovered).

Note on using ferrocene as internal standard. FCH is commonly used as an internal standard due to its chemical inertness, symmetry and convenient chemical shift. However one should note that FCH protons have extremely long relaxation time and in order to obtain the correct integration values the delay time (d1) should be set to at least 30 seconds. In all our experiments d1 was set to 60 s and acquisition time to 5 s. All spectra were measured at RT at a frequency 300 MHz.

The signals used for integration. The spectra of the complexes are given above (note that Tol-d₈ was chosen in certain cases to ensure better solubility and the chemical shifts in C₆D₆ and Tol-d₈ are slightly different but the corresponding peaks can be easily identified). All signals of known compounds, unless significantly overlapping, were integrated and used to cross-check the quantification (in most cases the results obtained from different peaks matched well (within 1–3%), otherwise we used the peak that had the least overlap with its neighbors). For benzophenone (abbreviated below as “bph”) very convenient for quantification is the downfield resonance at 7.65 ppm in Tol-d₈ (7.71 in C₆D₆). Similarly, for imines, besides the signals attributed to the imino group, we used the downfield resonances at 7.76 (Ph₂C=NtBu) and 7.89 ppm (Ph₂C=NAr). Note that for benzophenone this resonance accounts for 4 protons, whereas in the case of imines it is due to 2 protons (see **Fig. S12**). The spectra of benzophenone and imines are given below. Chemical shifts of other relevant compounds (pyridine, Me₂PyrH, ArNH₂, etc.) were either taken from literature or identified in other experiments.

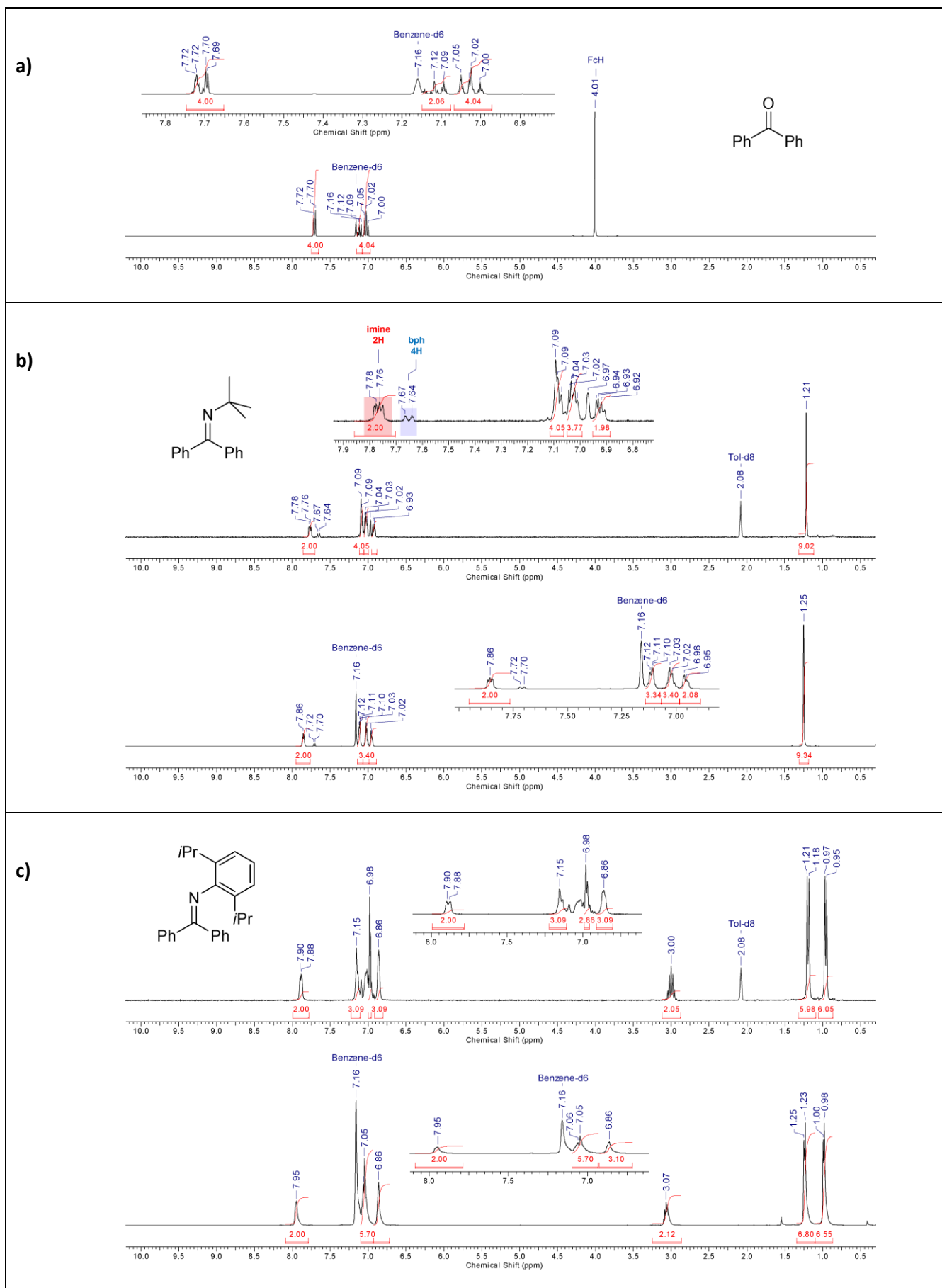
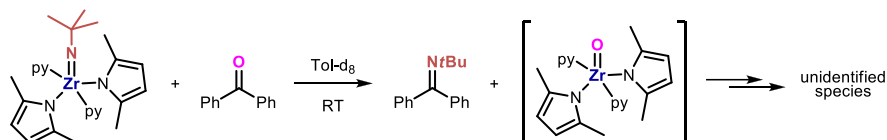


Fig. S14. ^1H NMR spectra of (a) Ph_2CO (in C_6D_6 ; with FcH added), (b) $\text{Ph}_2\text{C}=\text{NtBu}$ (in Tol-d_8 and C_6D_6 ; small amount of Ph_2CO added for comparison), (c) $\text{Ph}_2\text{C}=\text{NAr}$ (in Tol-d_8 and C_6D_6).

Reaction of $Zr(=NtBu)(Me_2Pyr)_2(py)_2$ (**1a**) with Ph_2CO



Loading: **1a** (15.6 mg, 30.7 μ mol), Ph_2CO (5.8 mg, 31.8 μ mol, 1.04 equiv/Zr), FcH (9.2 mg, 49.5 μ mol).

Table S1 ^a	10 min	1 h	5 h	24 h	3 days	5 days	7 days
cmplx reacted	59%	74%	80%	89%	91%	92%	92%
bph reacted/Zr	80%	97%	104%	104%	104%	104%	104%
imine formed/Zr	25%	32%	35%	37%	38%	36%	38%
Me ₂ PyrH/Zr	4%	8%	12%	25%	39%	45%	48%
py/Zr	n/d ^b	n/d ^b	n/d ^b	98%	115%	107%	100%

^a Values expressed in % relative to the initial amount of **1a**. ^b Difficult to integrate due to overlap.

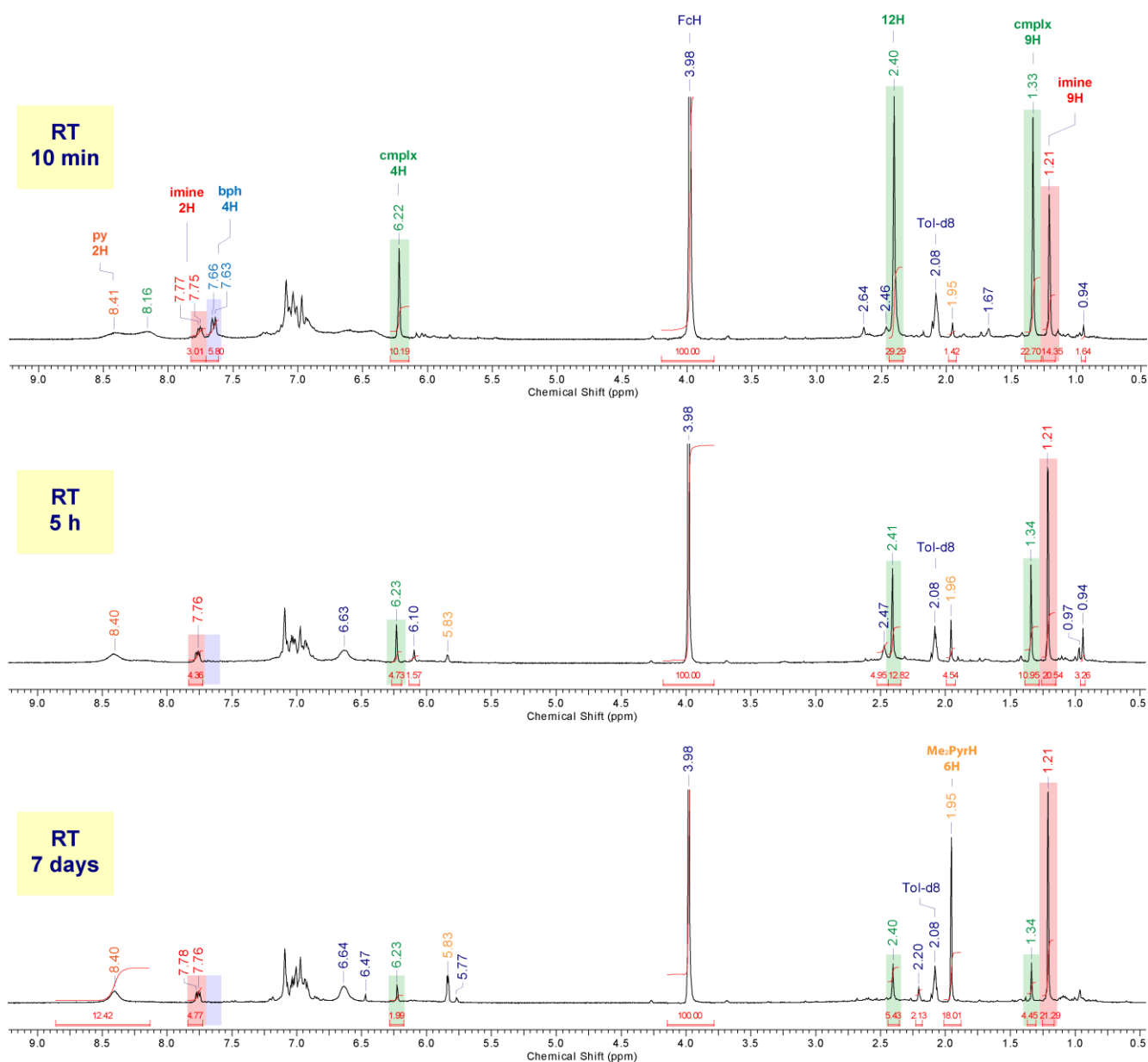
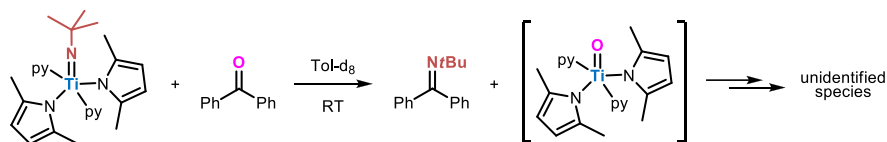


Fig. S15. Representative ¹H NMR spectra of the reaction of **1a** with Ph_2CO .

Reaction of Ti(=NtBu)(Me₂Pyr)₂(py)₂ (2a) with Ph₂CO



Loading: **2a** (14.1 mg, 30.3 μmol), Ph₂CO (5.7 mg, 31.3 μmol, 1.03 equiv/Ti), FcH (10.3 mg, 55.4 μmol).

Table S2 ^a	10 min	1 h	5 h	24 h	3 days	5 days	7 days
cmplx reacted	32%	51%	61%	84%	95%	97%	96%
bph reacted/Ti	36%	42%	50%	71%	88%	97%	101%
imine formed/Ti	1%	4%	11%	19%	26%	28%	29%
Me ₂ PyrH/Ti	1%	2%	6%	14%	31%	37%	46%
py/Ti	n/d ^b	n/d ^b	n/d ^b	94%	111%	116%	118%

^a Values expressed in % relative to the initial amount of **2a**. ^b Difficult to integrate due to overlap.

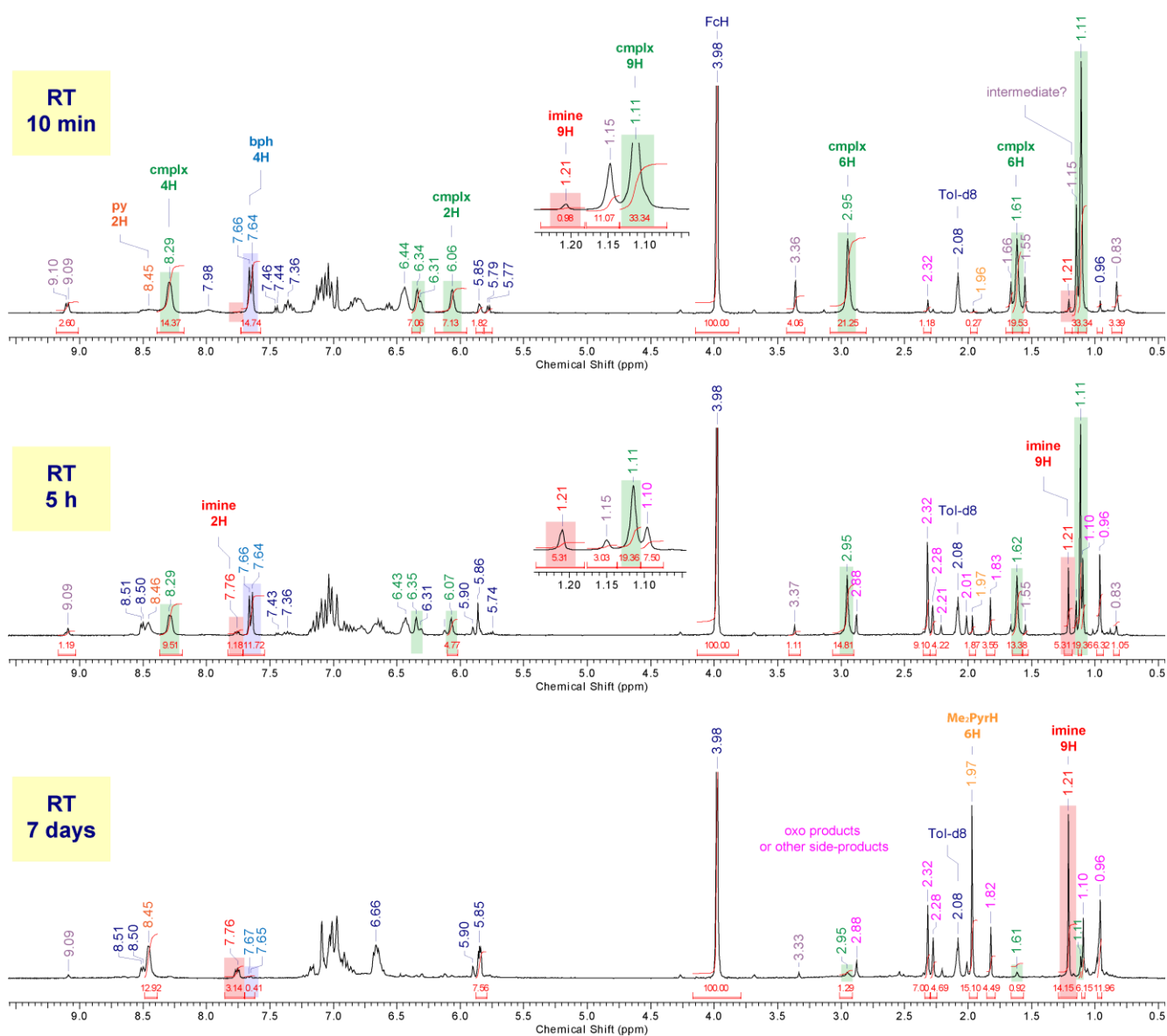
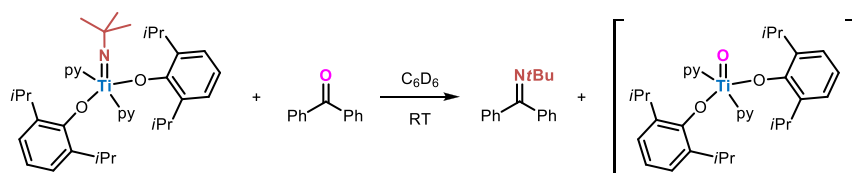


Fig. S16. Representative ¹H NMR spectra of the reaction of **2a** with Ph₂CO.

Reaction of $\text{Ti}(=\text{NtBu})(\text{OAr})_2(\text{py})_2$ (**2c**) with Ph_2CO



Loading: **2c** (23.5 mg, 37.2 μmol), Ph_2CO (8.0 mg, 43.9 μmol , 1.18 equiv/Ti), FcH (13.6 mg, 73.1 μmol).

Table S3 ^a	RT 1.5 h	RT 5 days	RT 11 days	RT 26 days
cmplx reacted	33%	72%	83%	88%
bph reacted/Ti	20%	64%	76%	89%
imine formed/Ti	17%	61%	70%	83%
"Ti oxo" product	9%	49%	57%	80%

^a Values expressed in % relative to the initial amount of **2c**.

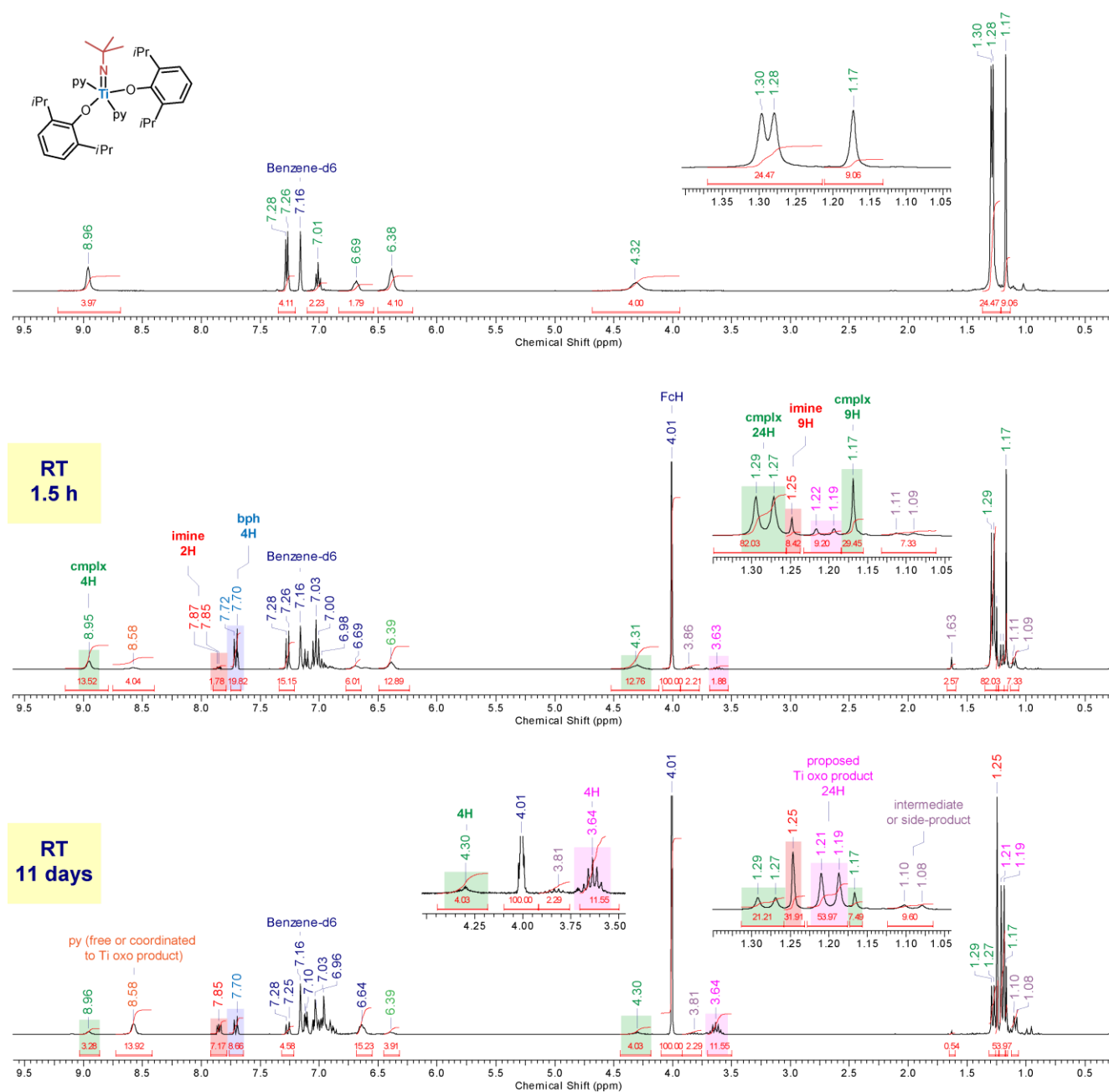
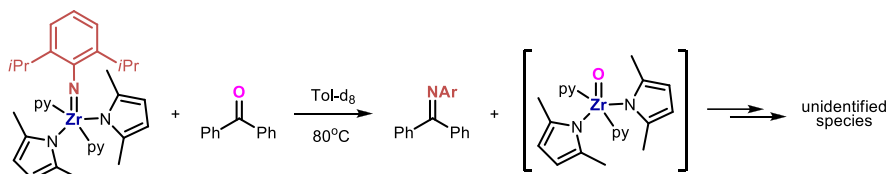


Fig. S17. Representative ^1H NMR spectra of the reaction of **2c** with Ph_2CO .

Reaction of Zr(=NAr)(Me₂Pyr)₂(py)₂ (**1b**) with Ph₂CO



Loading: **1b** (13.6 mg, 22.2 μmol), Ph₂CO (4.5 mg, 24.7 μmol, 1.11 equiv/Zr), FcH (11.3 mg, 60.7 μmol).

Table S4 ^a	RT 30 min	RT 24 h	50°C 1 h	80°C 1 h	80°C 1 day	80°C 2 days	80°C 3 days
cmplx reacted	4%	26%	28%	37%	64%	67%	69%
bph reacted/Zr	-	22%	31%	50%	105%	111%	111%
imine formed/Zr	-	4%	10%	19%	36%	38%	38%
Me ₂ PyrH/Zr	5%	10%	15%	23%	46%	52%	55%
py/Zr	13%	21%	30%	53%	87%	92%	100%

^a Values expressed in % relative to the initial amount of **1b**.

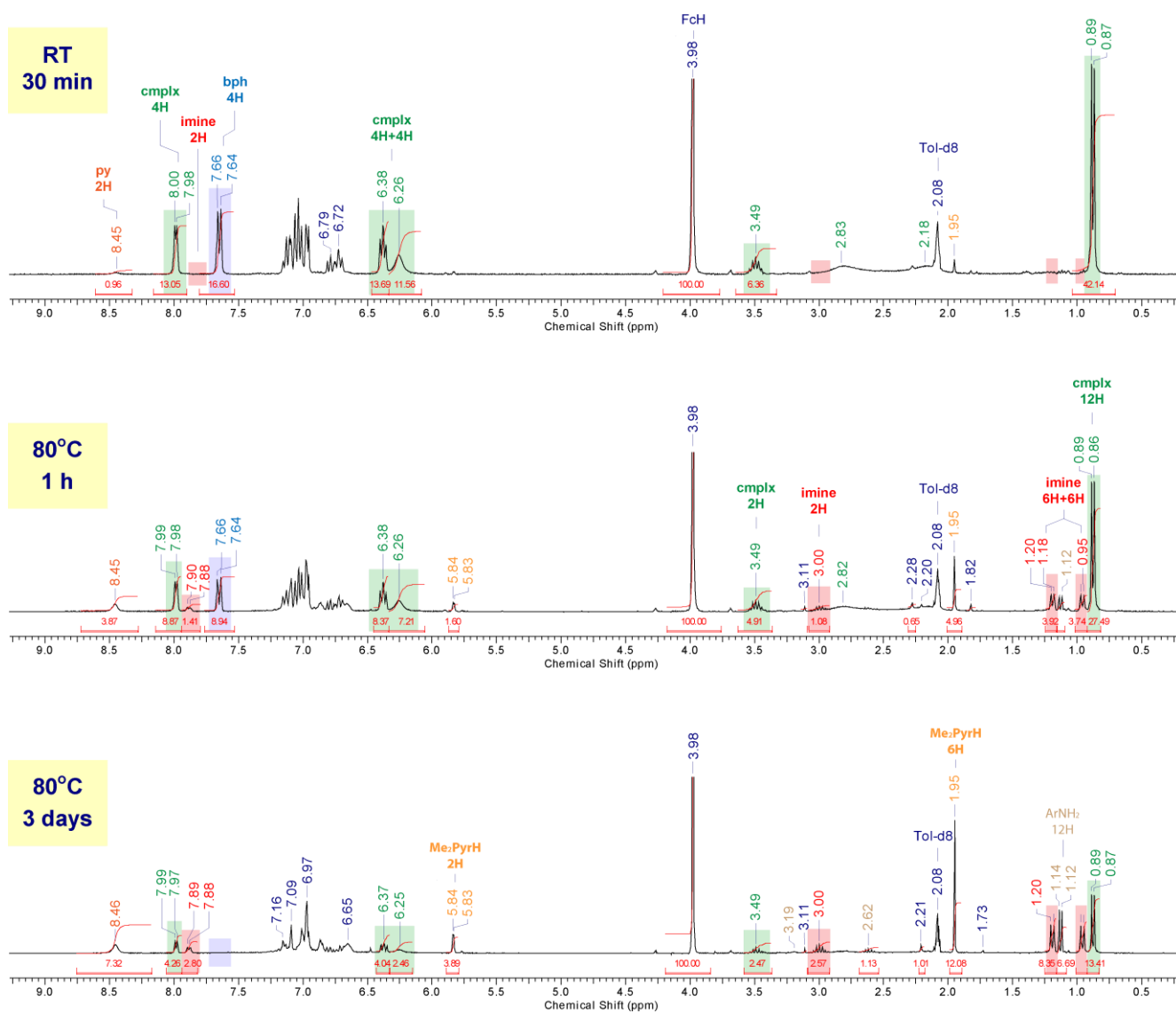
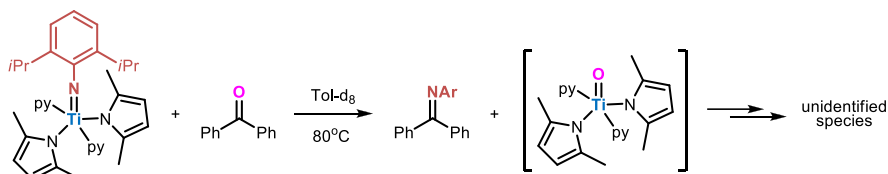


Fig. S18. Representative ¹H NMR spectra of the reaction of **1b** with Ph₂CO.

Reaction of $\text{Ti}(=\text{NAr})(\text{Me}_2\text{Pyr})_2(\text{py})_2$ (**2b**) with Ph_2CO



Loading: **2b** (12.3 mg, 21.6 μmol), Ph_2CO (4.2 mg, 23.0 μmol , 1.06 equiv/Ti), FcH (11.4 mg, 61.3 μmol).

Table S5 ^a	RT 30 min	RT 24 h	50°C 1 h	80°C 1 h	80°C 1 day	80°C 2 days	80°C 3 days
cmplx reacted	28%	30%	27%	34%	57%	65%	72%
bph reacted/Ti	17%	19%	18%	21%	61%	76%	87%
imine formed/Ti	-	-	-	6%	21%	27%	31%
$\text{Me}_2\text{PyrH}/\text{Ti}$	1%	2%	3%	6%	38%	52%	60%
py/Ti	20%	20%	21%	23%	59%	73%	83%

^a Values expressed in % relative to the initial amount of **2b**.

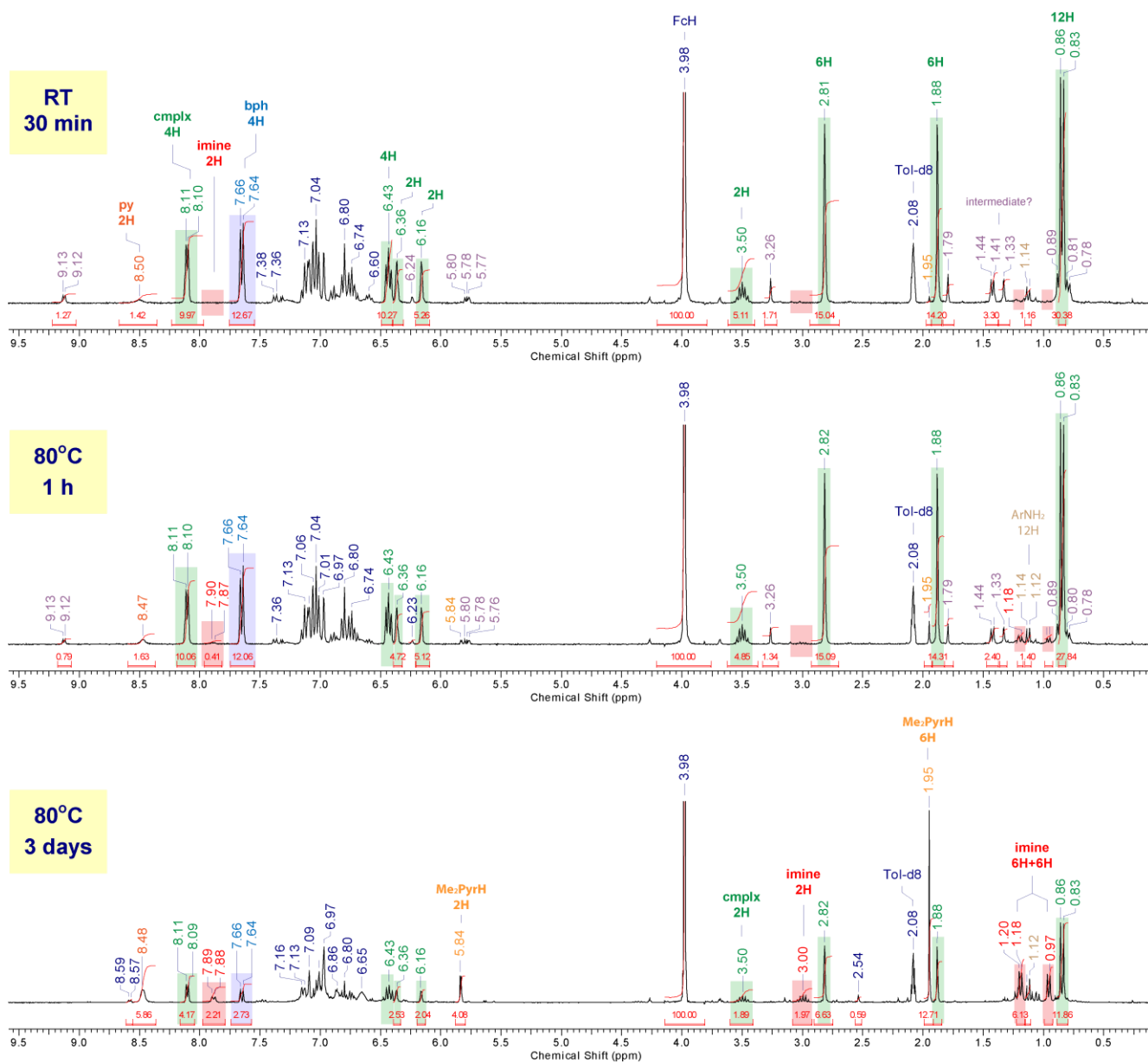


Fig. S19. Representative ^1H NMR spectra of the reaction of **2b** with Ph_2CO .

Observation of the intermediate in the reaction of $\text{Ti}(\text{=NAr})(\text{Me}_2\text{Pyr})_2(\text{py})_2$ (**2b**) with Ph_2CO

When **2b** is treated with excess Ph_2CO (4–5 equiv) the concentration of the intermediate can be increased by *in situ* removal of pyridine *via* several consecutive evaporation/redissolution cycles. This allowed us to characterize the intermediate (that we propose to be a coordination adduct or a metallacycle resulting from [2+2] cycloaddition of Ph_2CO across $\text{Ti}=\text{NAr}$ bond) with ^1H NMR spectroscopy, but only in the presence of excess Ph_2CO . Unfortunately, the attempts to remove benzophenone, isolate and further characterize this species led to decomposition. The intermediate possesses lower symmetry than the initial complex **2b**, which is manifested in the appearance of 4 distinct resonances of pyrrolyl methyl groups and 2 doublets for CHMe_2 groups, although this information is still not sufficient to make final assignment.

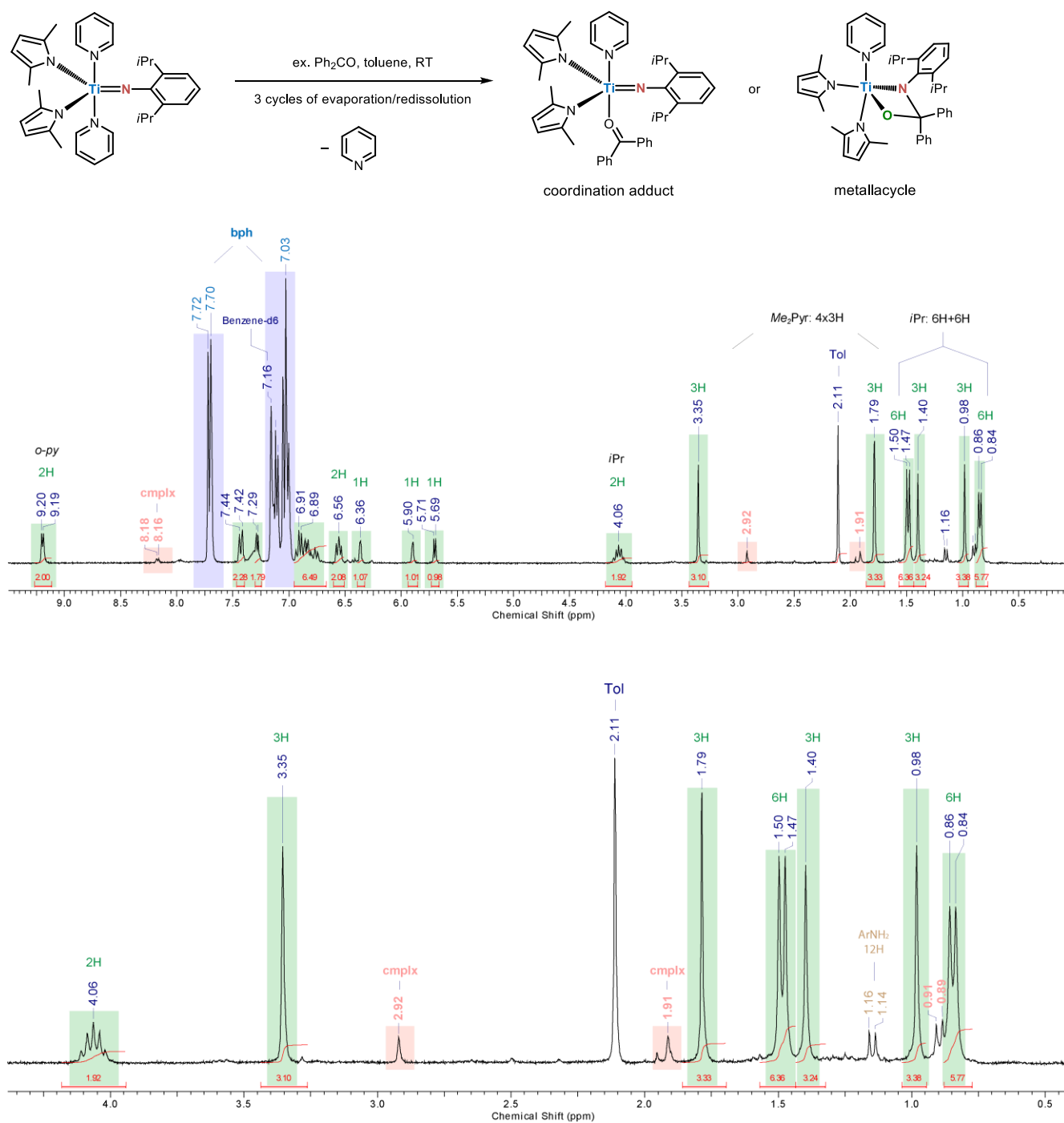
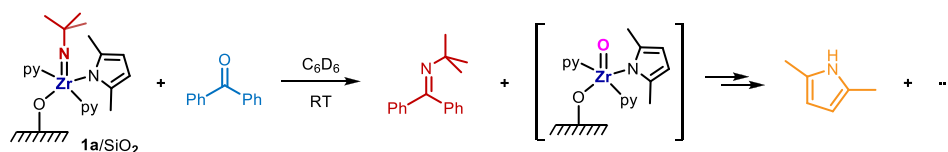


Fig. S20. ^1H NMR spectrum of the intermediate observed in the reaction between **2b** and Ph_2CO .

Reactions of grafted complexes with Ph₂CO



Loading: 1a/SiO₂ (17.0 mg, 3.9 μmol), Ph₂CO (3.2 mg, 17.6 μmol, 4.5 equiv/Zr), FcH (13.2 mg, 71.0 μmol).

Table S6 ^a	1 h	24 h	3 days	4 days	6 days
bph reacted/Zr _{surf}	51%	102%	124%	119%	115%
imine formed/Zr _{surf}	27%	39%	45%	47%	48%
Me ₂ PyrH/Zr _{surf}	8%	23%	38%	42%	48%

^a Values expressed in % relative to the total amount of Zr_{surf}.

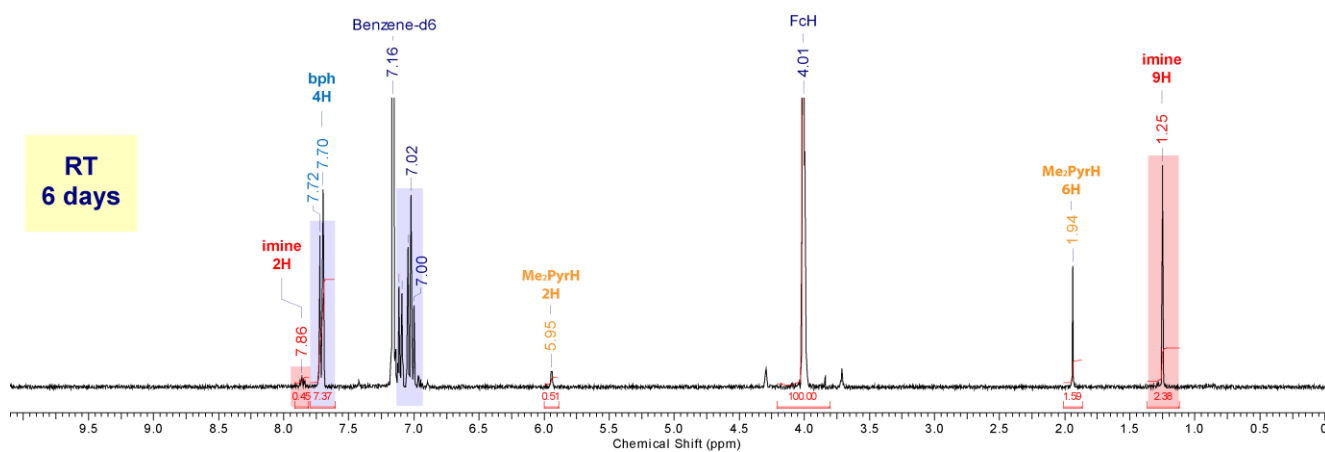
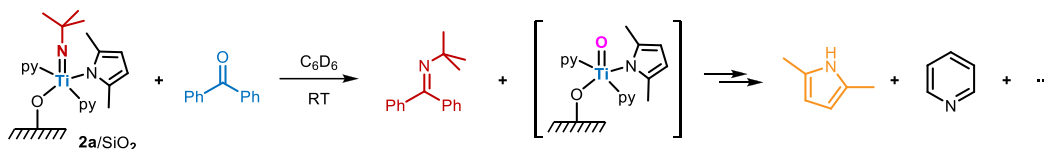


Fig. S21. Representative ¹H NMR spectrum of the reaction of 1a/SiO₂ with Ph₂CO.



Loading: **2a/SiO₂** (16.7 mg, 3.8 μmol), **Ph₂CO** (2.6 mg, 14.3 μmol, 3.8 equiv/Ti), **FcH** (9.2 mg, 49.5 μmol).

Table S7^a	1 h	24 h	3 days	4 days	6 days
bph reacted/Ti_{surf}	56%	108%	134%	133%	145%
imine formed/Ti_{surf}	21%	57%	67%	72%	74%
Me₂PyrH/Ti_{surf}	30%	44%	49%	50%	50%

^a Values expressed in % relative to the total amount of Ti_{surf}.

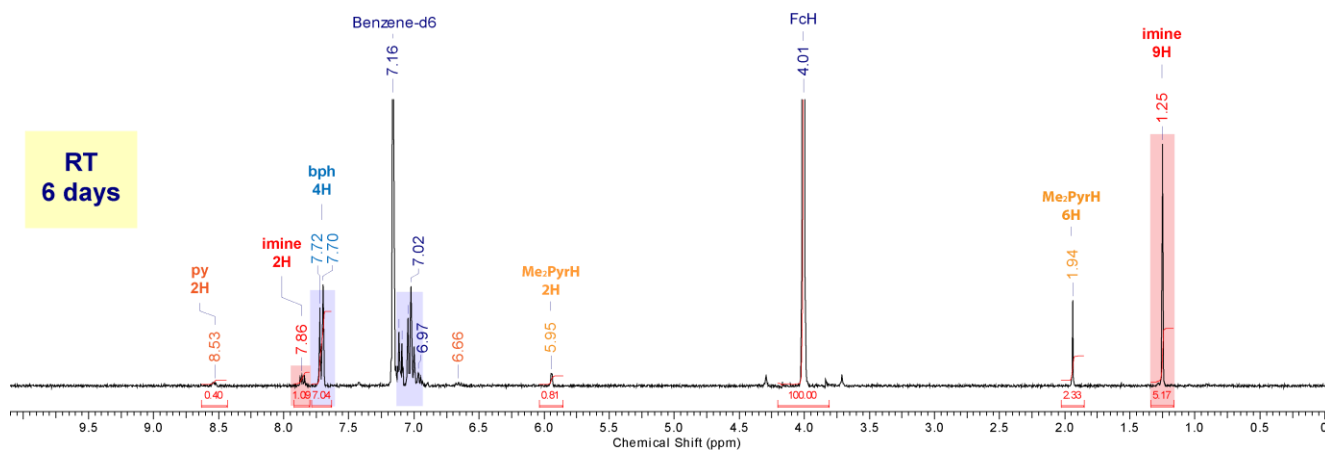
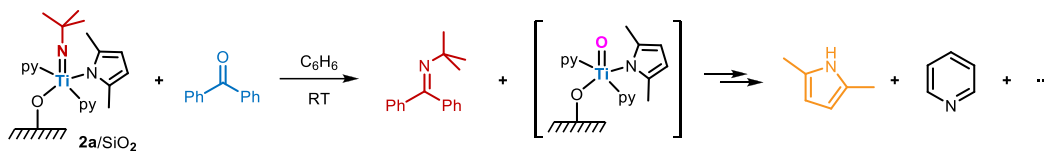


Fig. S22. Representative ¹H NMR spectra of the reaction of **2a/SiO₂** with **Ph₂CO**.



The reaction was repeated on a larger scale (104 mg **2a/SiO₂** and 22.5 mg Ph_2CO). After the reaction the solid was washed with C_6H_6 , dried in high vacuum and analyzed with IR (**Fig. S23**) and solid-state NMR (**Fig. S24, S25**).

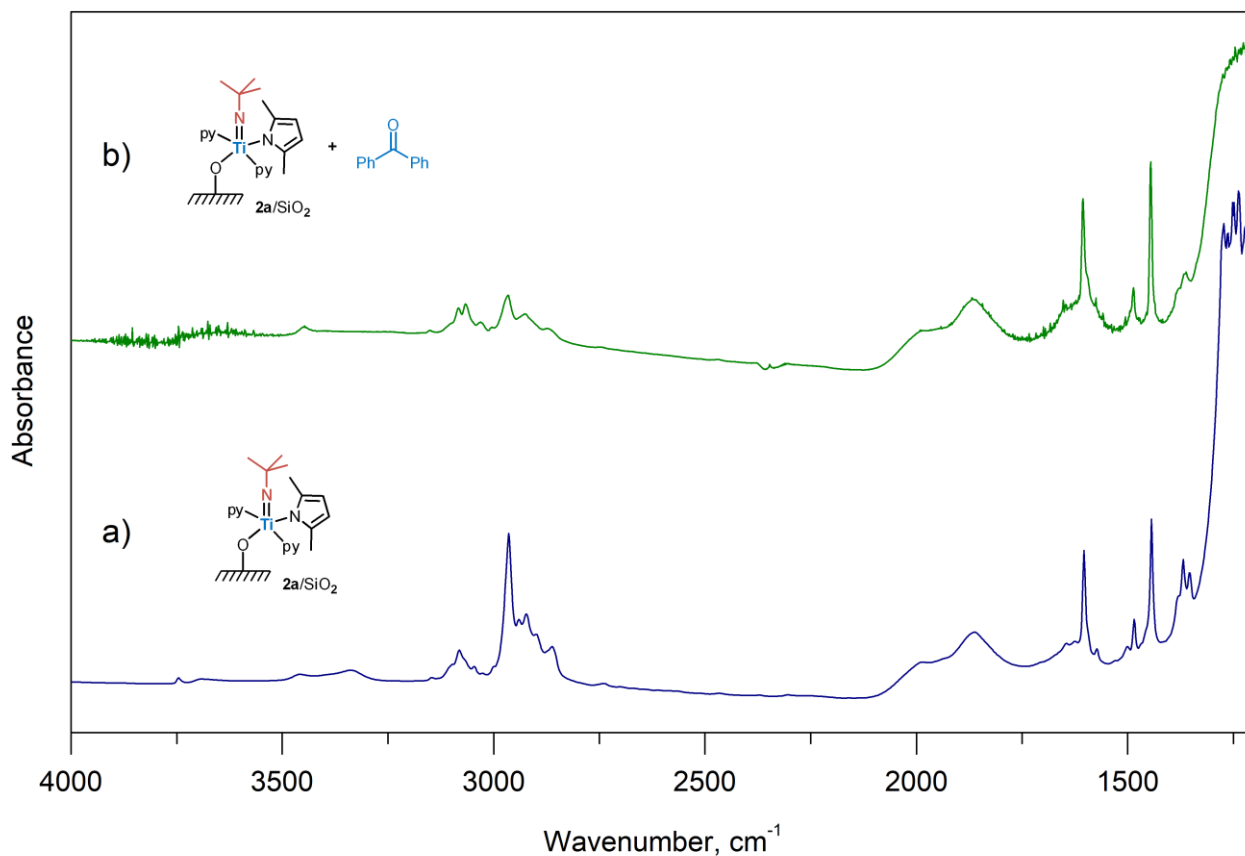


Fig. S23. IR spectra of (a) **2a/SiO₂**, and (b) **2a/SiO₂** after the reaction with Ph_2CO . Spectrum (b) was recorded at Shimadzu IRTracer-100 instrument operated in air; the sample was pressed into a pellet inside a glovebox and transferred to the spectrometer in a home-made air-tight cell.

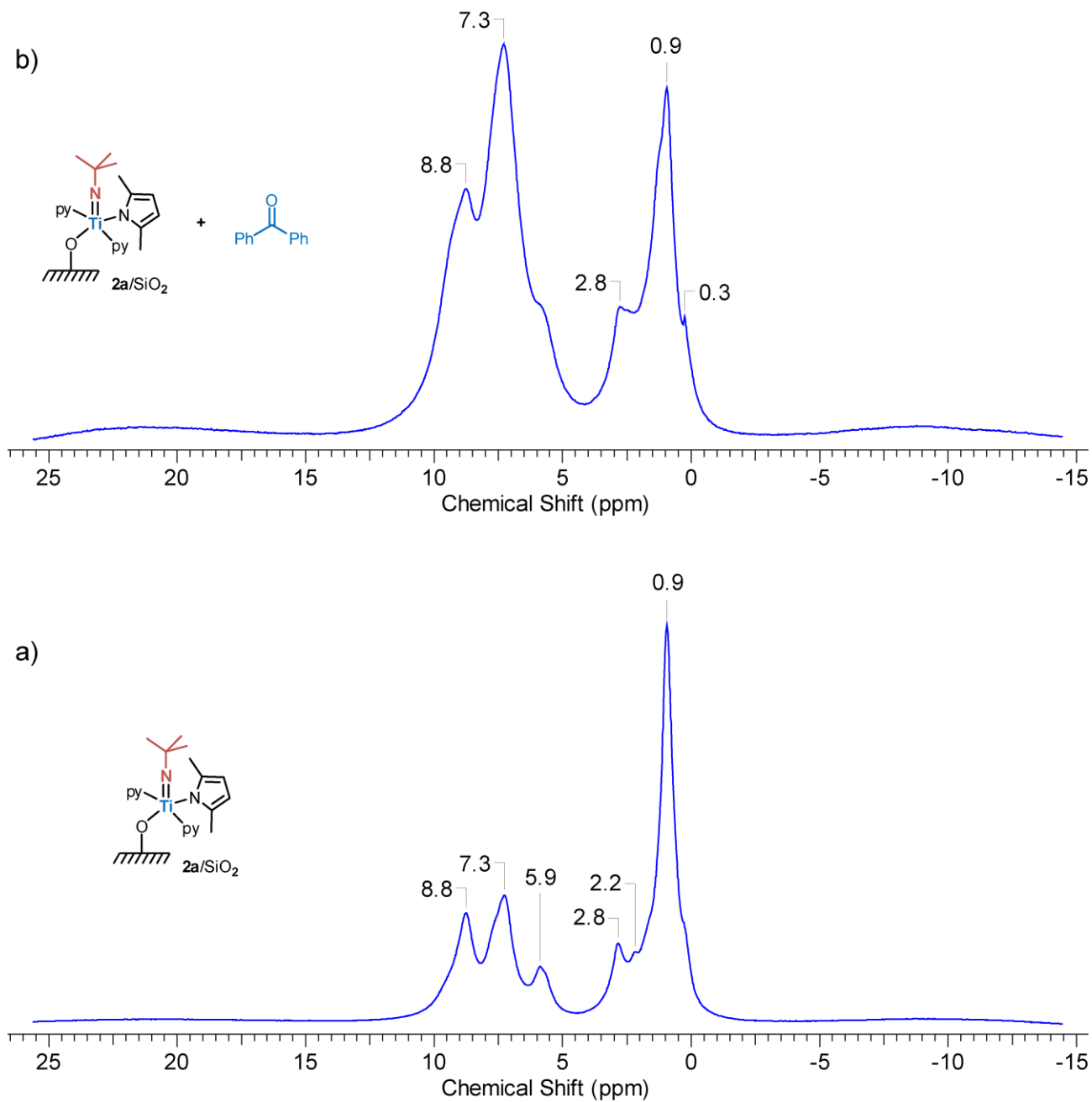


Fig. S24. ^1H MAS solid-state NMR spectra of (a) **2a**/ SiO_2 (400 MHz; 14 kHz MAS), and (b) **2a**/ SiO_2 after the reaction with Ph_2CO (400 MHz; 12 kHz MAS).

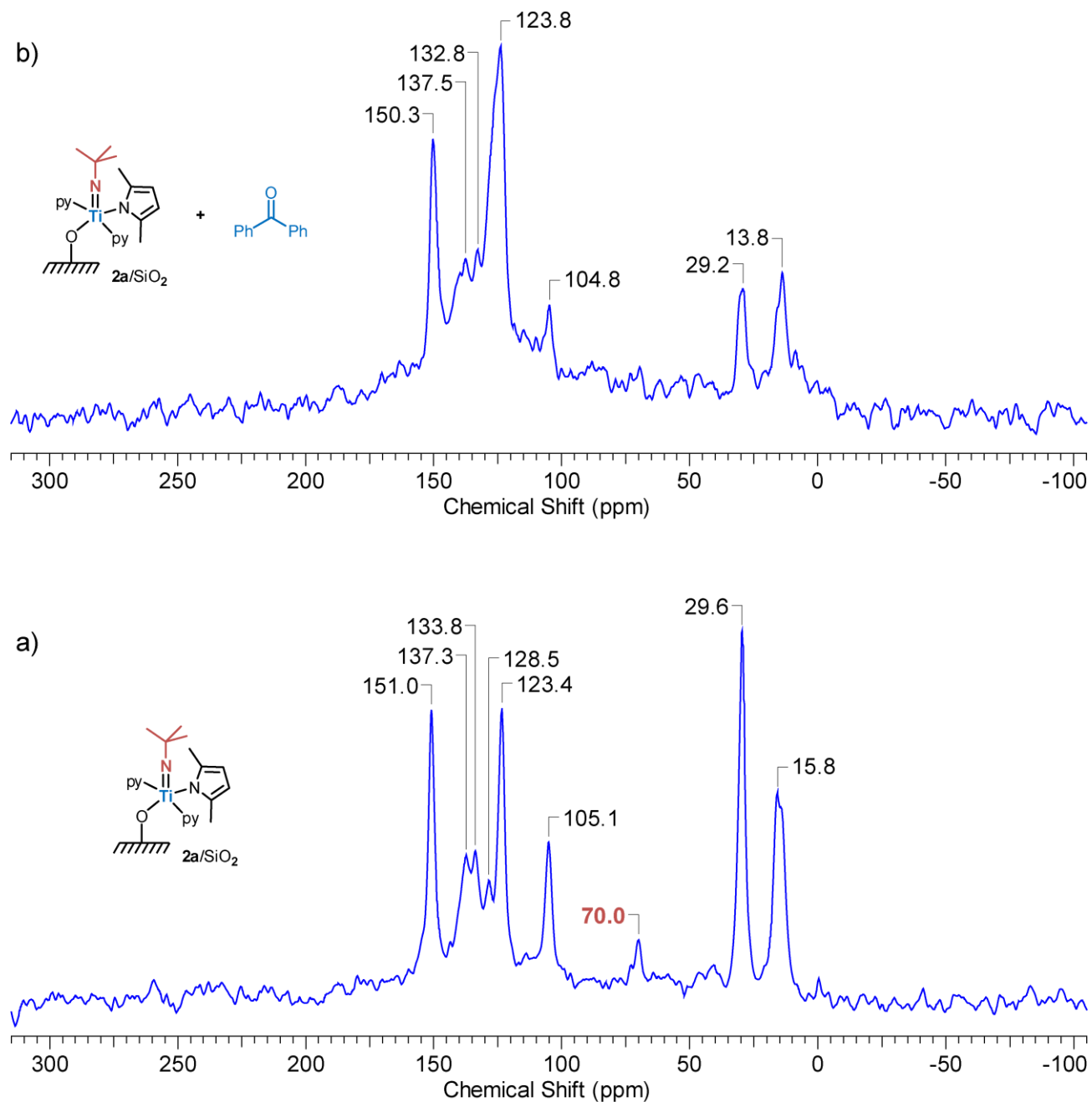
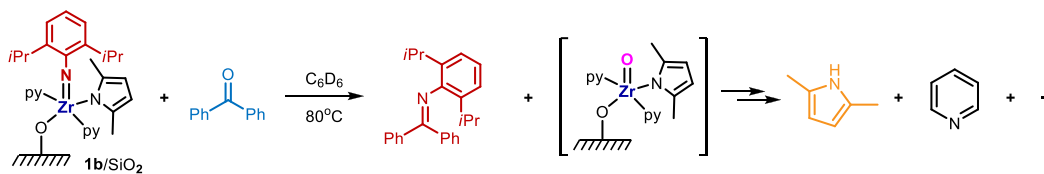


Fig. S25. ^{13}C CP MAS solid-state NMR spectra of (a) **2a**/ SiO_2 (100 MHz; 11 kHz MAS; CP contact time 3 ms; recycle delay 2.5 s; 19'000 scans), and (b) **2a**/ SiO_2 after the reaction with Ph_2CO (100 MHz; 12 kHz MAS; CP contact time 4 ms; recycle delay 2 s; 24'000 scans).



Loading: **1b**/SiO₂ (14.8 mg, 3.2 μmol), Ph₂CO (1.9 mg, 10.4 μmol, 3.3 equiv/Zr), FcH (9.4 mg, 50.5 μmol).

Table S8 ^a	RT, 1 h	RT, 24 h	80°C, 24 h
bph reacted/Zr_{surf}	44%	80%	164%
imine formed/Zr_{surf}	-	30%	69%
Me₂PyrH/Zr_{surf}	4%	10%	26%

^a Values expressed in % relative to the total amount of Zr_{surf}.

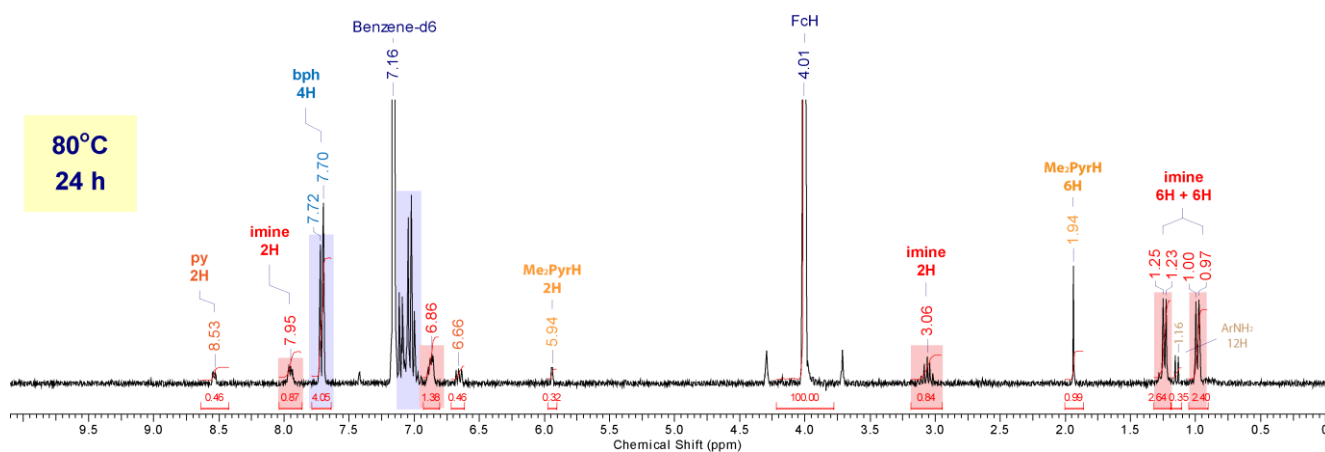
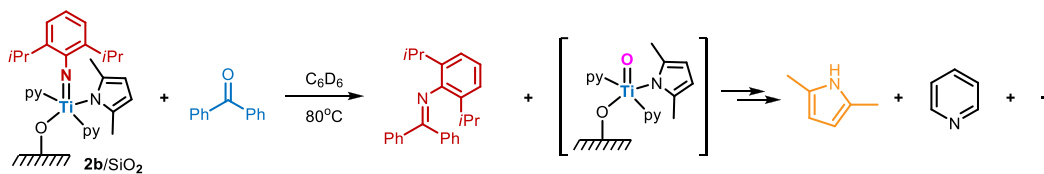


Fig. S26. Representative ¹H NMR spectra of the reaction of **1b**/SiO₂ with Ph₂CO.



Loading: 2b/SiO₂ (14.3 mg, 3.2 μmol), Ph₂CO (2.9 mg, 15.9 μmol, 5.0 equiv/Ti), FcH (9.5 mg, 51.1 μmol).

Table S9 ^a	RT, 1 h	RT, 24 h	80°C, 24 h
bph reacted/Ti _{surf}	-	3%	146%
imine formed/Ti _{surf}	-	15%	91%
Me ₂ PyrH/Ti _{surf}	8%	14%	26%

^a Values expressed in % relative to the total amount of Ti_{surf}.

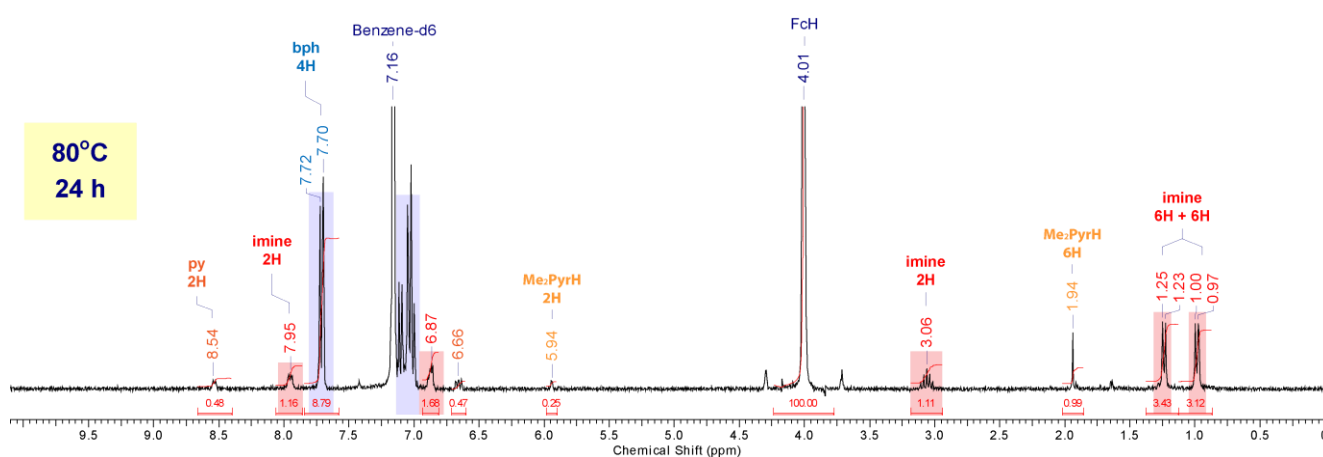


Fig. S27. Representative ¹H NMR spectra of the reaction of 2b/SiO₂ with Ph₂CO.

Computational Details

Computational studies were carried out at Euler Cluster of ETH Zürich. DFT calculations were performed with the Gaussian09 (revision D.01) package^[2] using the PBE0 functional,^[3] Def2-TZVP^[4, 5] basis set for non-metal atoms and SDD functional with the corresponding effective core potential for Ti and Zr.^[6] Natural population analysis was performed with NBO 5.9 integrated in Gaussian.^[7] MO images were created in GaussView 6.0. All images are Kohn-Sham orbitals at isovalue 0.05. MO compositions were analyzed in Chemissian^[8] using scheme “simple” (*i.e.* with AO contributions estimated as $C_i^2 / \sum C_j^2$).

Molecular Orbitals

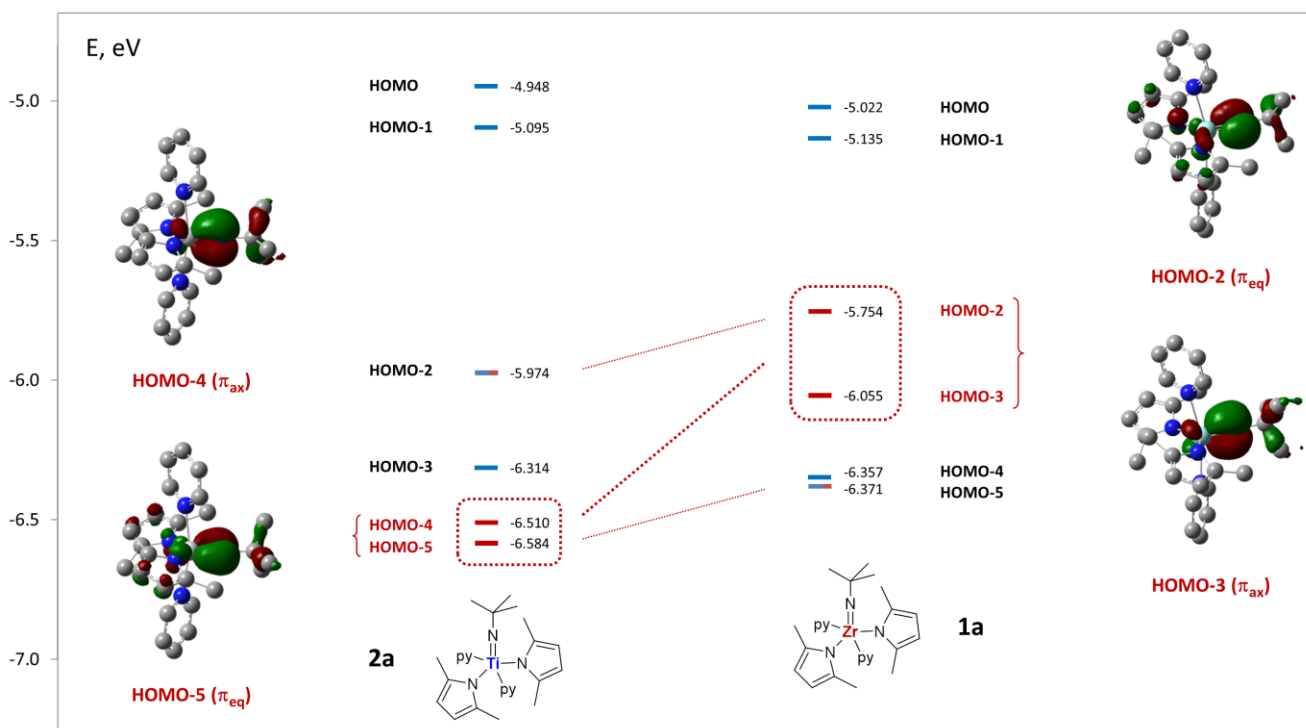


Fig. S28. Highest occupied molecular orbitals of Ti and Zr complexes **2a** and **1a**.

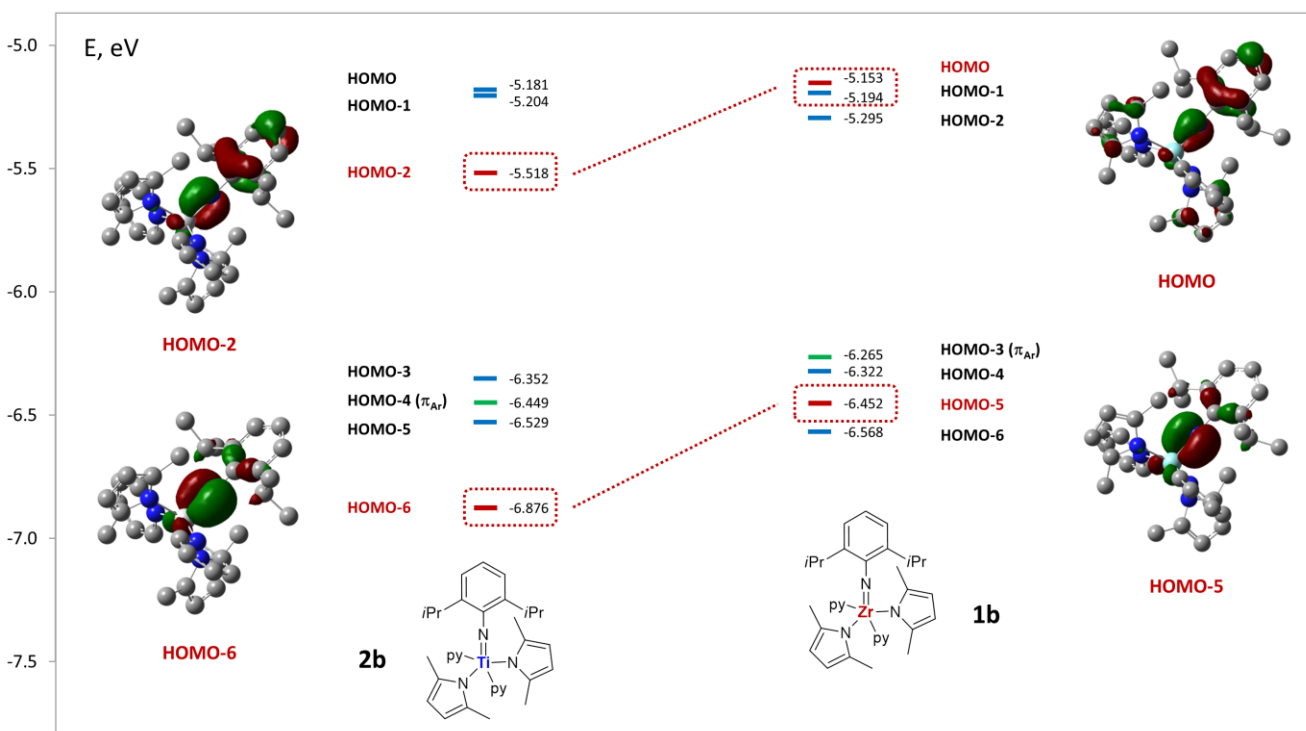
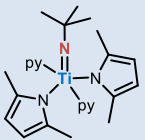
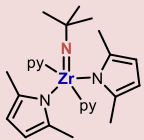


Fig. S29. Highest occupied molecular orbitals of Ti and Zr complexes **2b** and **1b**.

Table S10. Compositions and shapes of selected molecular orbitals of complexes **1a** and **2a**.

 $\text{Ti}(=\text{NtBu})(\text{Me}_2\text{Pyr})_2(\text{py})_2$ (2a)								 $\text{Zr}(=\text{NtBu})(\text{Me}_2\text{Pyr})_2(\text{py})_2$ (1a)							
MO	E, eV	Ti	N _{imido}	tBu	Me ₂ Pyr	other		MO	E, eV	Zr	N _{imido}	tBu	Me ₂ Pyr	other	
119	HOMO	-4.948	3%	-	-	95%	2%	119	HOMO	-5.022	2%	-	-	97%	1%
118	HOMO-1	-5.095	1%	-	-	97%	2%	118	HOMO-1	-5.135	2%	-	-	96%	2%
117	HOMO-2	-5.974	6%	12%	5%	67%	10%	117	HOMO-2	-5.754	12%	27%	10%	47%	4%
116	HOMO-3	-6.314	11%	1%	1%	80%	7%	116	HOMO-3	-6.055	23%	39%	15%	14%	9%
115	HOMO-4	-6.510	30%	43%	17%	3%	7%	115	HOMO-4	-6.357	13%	-	-	77%	10%
114	HOMO-5	-6.584	21%	31%	13%	30%	5%	114	HOMO-5	-6.371	10%	10%	5%	65%	11%

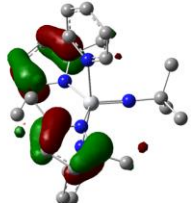
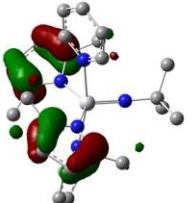
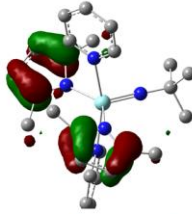
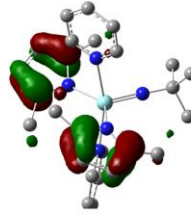
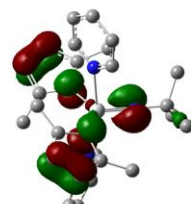
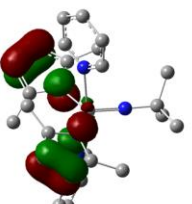
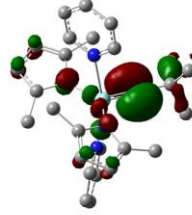
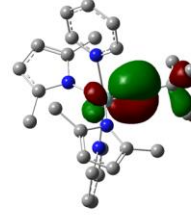
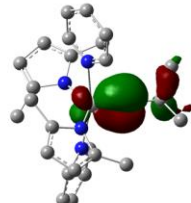
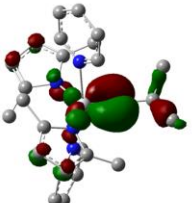
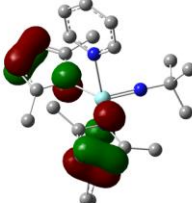
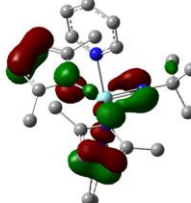
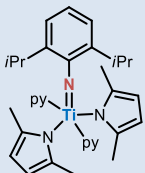
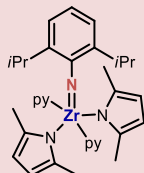
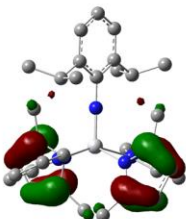
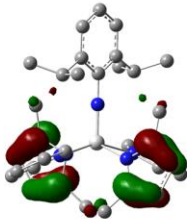
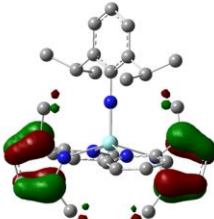
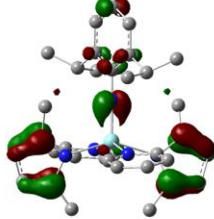
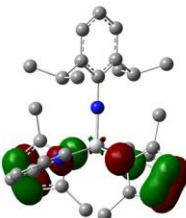
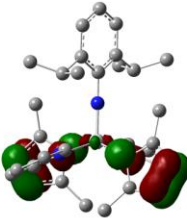
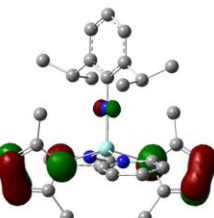
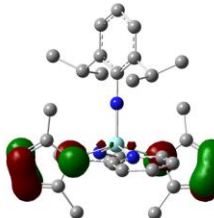
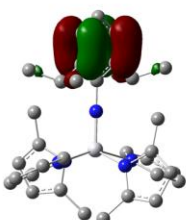
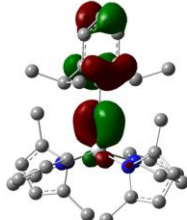
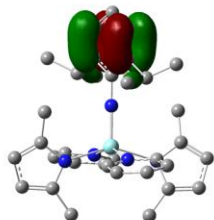
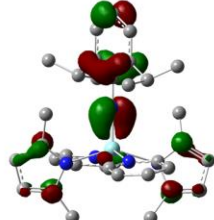
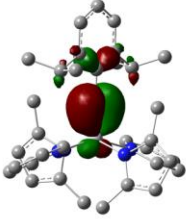
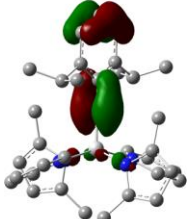
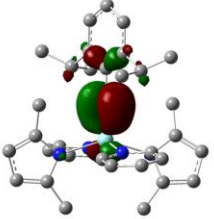
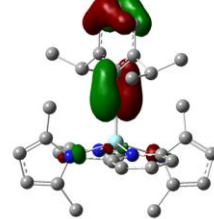
			
119 (HOMO)	118 (HOMO-1)	119 (HOMO)	118 (HOMO-1)
			
117 (HOMO-2)	116 (HOMO-3)	117 (HOMO-2)	116 (HOMO-3)
			
115 (HOMO-4)	114 (HOMO-5)	115 (HOMO-4)	114 (HOMO-5)

Table S11. Compositions and shapes of selected molecular orbitals of complexes **1b** and **2b**.

 $\text{Ti(=NAr)(Me}_2\text{Pyr)}_2(\text{py})_2$ (2b)								 $\text{Zr(=NAr)(Me}_2\text{Pyr)}_2(\text{py})_2$ (1b)							
MO	E, eV	Ti	N _{imido}	Ar	Me ₂ Pyr	other		MO	E, eV	Zr	N _{imido}	Ar	Me ₂ Pyr	other	
147	HOMO	-5.191	2%	-	7%	89%	2%	147	HOMO	-5.163	9%	13%	34%	42%	2%
146	HOMO-1	-5.194	3%	-	5%	89%	3%	146	HOMO-1	-5.184	3%	-	1%	92%	4%
145	HOMO-2	-5.518	20%	18%	50%	9%	3%	145	HOMO-2	-5.295	6%	6%	17%	68%	2%
144	HOMO-3	-6.352	4%	-	8%	75%	13%	144	HOMO-3	-6.265	-	-	97%	2%	1%
143	HOMO-4	-6.449	-	-	96%	2%	2%	143	HOMO-4	-6.322	7%	3%	2%	76%	12%
142	HOMO-5	-6.529	10%	-	4%	77%	9%	142	HOMO-5	-6.452	11%	26%	49%	12%	2%
141	HOMO-6	-6.876	24%	40%	28%	2%	6%	141	HOMO-6	-6.568	11%	-	1%	80%	8%
138	HOMO-9	-8.339	6%	24%	38%	30%	2%	140	HOMO-7	-8.006	6%	24%	44%	23%	3%

			
147 (HOMO)	146 (HOMO-1)	146 (HOMO-1)	145 (HOMO-2)
			
144 (HOMO-3)	142 (HOMO-5)	143 (HOMO-4)	141 (HOMO-6)
			
143 (HOMO-4)	145 (HOMO-2)	144 (HOMO-3)	147 (HOMO)
			
141 (HOMO-6)	138 (HOMO-9)	142 (HOMO-5)	140 (HOMO-7)

Optimized Geometries

Zr(=NtBu)(Me ₂ Pyr) ₂ (py) ₂ (1a)				Ti(=NtBu)(Me ₂ Pyr) ₂ (py) ₂ (2a)			
E = -1331.69272031 a.u.				E = -1342.93358618 a.u.			
Atom	x	y	z	Atom	x	y	z
Zr	-0.00476	-0.079358	0.147001	Ti	0.000704	0.018688	0.149119
N	-2.290989	-0.462306	-0.455188	N	-0.355041	1.644671	-1.094641
N	0.573252	-1.299436	-1.630369	N	0.398345	-1.998341	-0.164345
N	0.044064	-1.076927	1.682466	N	-2.171491	-0.509661	-0.061547
N	-0.607755	2.038358	0.52672	C	0.993575	0.762401	-3.070274
N	2.26776	0.678834	0.168268	H	1.983954	1.206106	-2.917731
C	0.418812	-0.778934	-2.905879	H	0.828242	0.703153	-4.147674
C	-2.706134	-1.726166	-0.583879	H	1.044973	-0.263022	-2.697434
H	-1.969203	-2.493049	-0.375892	N	2.184863	0.415931	-0.188965
C	2.696319	1.34339	1.245574	N	-0.051366	0.432539	1.777618
H	1.973533	1.473855	2.042434	C	-0.121742	0.850623	3.154663
C	1.336603	-1.351774	-3.754454	C	-2.639887	-1.455102	0.758157
H	1.424877	-1.156659	-4.814046	H	-1.921589	-1.88096	1.447603
C	-1.453143	3.954956	-0.316572	C	2.627082	1.641759	0.106272
H	-1.586596	4.82348	-0.946253	H	1.884379	2.334697	0.480607
C	2.053827	-3.015371	-0.528793	C	-4.820286	-1.313106	-0.188519
H	2.56425	-2.398857	0.217845	H	-5.856841	-1.626827	-0.237873
H	2.752883	-3.786392	-0.857733	C	-0.080284	1.597358	-2.455618
H	1.222258	-3.505459	-0.015757	C	1.686358	-3.844331	-0.302925
C	-2.153964	3.641084	0.872772	H	2.383308	-4.625041	-0.032386
H	-2.955615	4.205571	1.328093	C	-4.335793	-0.338758	-1.043005
C	-3.993286	-2.05136	-0.964671	H	-4.970889	0.13438	-1.780976
H	-4.280892	-3.090954	-1.055106	C	3.94486	2.019942	-0.061491
C	-3.153051	0.527364	-0.708713	H	4.251089	3.02644	0.193481
H	-2.781795	1.541202	-0.591532	C	0.996067	-3.696213	-1.528439
C	-0.714563	0.114288	-3.286832	H	1.030417	-4.354672	-2.385046
H	-1.648198	-0.44897	-3.398422	C	1.297903	-2.803692	0.506988
H	-0.502873	0.590218	-4.245966	C	0.209246	-2.575089	-1.413952
H	-0.918921	0.919452	-2.574327	C	-0.821162	2.552506	-3.109343
C	0.590988	2.961822	-1.50275	H	-0.786543	2.756064	-4.170381
H	1.534327	3.31153	-1.067917	C	4.846252	1.091704	-0.559231
H	0.340799	3.634521	-2.325047	H	5.887937	1.355686	-0.702639
H	0.79609	1.983627	-1.949236	C	-1.261145	2.672726	-0.913616
C	1.588803	-2.230503	-1.704115	C	4.388925	-0.175262	-0.874117
C	4.411814	0.968903	-0.826658	H	5.050789	-0.934036	-1.271624
H	5.058196	0.794699	-1.677263	C	3.051088	-0.475293	-0.678042
C	-4.460954	0.283891	-1.09261	H	2.656961	-1.45859	-0.911678
H	-5.123	1.11855	-1.284274	C	-1.819867	3.056534	0.408791
C	-1.61318	2.475497	1.364474	H	-2.441162	2.271055	0.848481
C	-4.889726	-1.025418	-1.222708	H	-2.440246	3.947215	0.293285
H	-5.90797	-1.245969	-1.522461	H	-1.035633	3.284226	1.134861
C	-0.5107	2.969729	-0.495782	C	1.758491	-2.539285	1.89448
C	0.10463	-1.89791	2.858645	H	2.224661	-1.55625	2.003948
C	3.110061	0.497856	-0.85353	H	2.490782	-3.295529	2.183145

H	2.727198	-0.047785	-1.710785
C	-2.011265	1.747026	2.598633
H	-2.395226	0.742994	2.394548
H	-2.792716	2.306276	3.116171
H	-1.170745	1.624669	3.286429
C	-0.518273	-1.18047	4.059502
H	0.010007	-0.246044	4.261887
H	-0.466193	-1.805218	4.956489
H	-1.566045	-0.943595	3.866406
C	2.07989	-2.281484	-2.988171
H	2.876742	-2.925095	-3.333587
C	4.8549	1.653611	0.291338
H	5.86894	2.033909	0.340144
C	3.978342	1.84685	1.348129
H	4.277615	2.378807	2.242071
C	1.564077	-2.223293	3.191598
H	2.03152	-2.780578	2.378731
H	1.632158	-2.822495	4.104794
H	2.130833	-1.301547	3.345051
C	-0.661277	-3.202544	2.617821
H	-1.709668	-2.98884	2.394454
H	-0.625466	-3.850571	3.498887
H	-0.232325	-3.746876	1.773656

H	0.935754	-2.578658	2.612052
C	-1.568821	3.24143	-2.126536
H	-2.250556	4.066278	-2.279222
C	-0.830924	-2.139573	-2.39171
H	-1.827309	-2.48954	-2.09895
H	-0.608416	-2.573386	-3.368365
H	-0.903604	-1.058476	-2.531535
C	-3.005375	0.034626	-0.951215
H	-2.589828	0.797118	-1.601524
C	-3.95253	-1.884102	0.729438
H	-4.280762	-2.654576	1.415337
C	-1.571802	1.170964	3.531214
H	-1.96039	1.999449	2.940567
H	-1.636255	1.442774	4.588753
H	-2.21055	0.300492	3.364662
C	0.379765	-0.249911	4.092821
H	-0.219923	-1.155259	3.980289
H	0.30617	0.080608	5.132859
H	1.420748	-0.499071	3.88535
C	0.749465	2.093477	3.358016
H	1.791945	1.869167	3.120438
H	0.702254	2.431273	4.397326
H	0.416712	2.912604	2.717702

Zr(=NAr)(Me ₂ Pyr) ₂ (py) ₂ (1b)			
E = -1641.11747040 a.u.			
Atom	x	y	z
Zr	0.000004	-0.678061	-0.000008
N	-0.000015	1.164572	0.000013
N	-2.209755	-1.14567	-0.799934
N	0.793381	-1.317599	-1.988102
N	2.209769	-1.14564	0.799922
N	-0.793358	-1.317677	1.988074
C	-2.440478	-1.400323	-2.093551
H	-1.564537	-1.423648	-2.731875
C	-0.000033	2.534919	0.000033
C	1.240629	-0.485244	-3.005911
C	1.193244	4.643175	-0.007012
H	2.128908	5.191837	-0.011696
C	-0.000082	5.344576	0.000117
H	-0.000102	6.428627	0.000154
C	-1.240624	-0.485355	3.005903
C	1.2214	3.255636	-0.00629
C	-1.221492	3.25559	0.006385
C	-2.537973	2.517511	-0.039701
H	-2.347615	1.521191	0.369176
C	-3.709121	-1.627702	-2.591637
H	-3.841424	-1.83059	-3.646592

Ti(=NAr)(Me ₂ Pyr) ₂ (py) ₂ (2b)			
E = -1652.35460005 a.u.			
Atom	x	y	z
Ti	0.002327	-0.614346	-0.000018
N	-0.018827	-1.222891	1.977507
N	0.028181	-1.222793	-1.977495
N	2.201476	-1.127699	0.012259
C	-0.94068	-3.56839	1.620144
H	-2.019689	-3.497997	1.799269
H	-0.625816	-4.565658	1.932973
H	-0.803733	-3.511307	0.539045
N	-2.192726	-1.144282	-0.012309
N	-0.004118	1.080282	-0.000083
C	-0.009407	2.457632	-0.00003
C	2.926389	-0.865332	-1.082146
H	2.389044	-0.417723	-1.907975
C	-2.919518	-0.887436	1.082154
H	-2.385469	-0.435838	1.907958
C	4.903009	-1.758447	-0.098211
H	5.957661	-2.005861	-0.1414
C	-0.18446	-2.537533	2.390758
C	-0.790152	-1.427089	-4.067163
H	-1.244128	-1.176114	-5.015355
C	4.156646	-2.037499	1.032228

C	2.537917	2.517624	0.03972	H	4.598257	-2.507661	1.901487
H	2.347574	1.521281	-0.369103	C	-4.263137	-1.191728	1.177259
C	2.440506	-1.400287	2.093538	H	-4.799759	-0.960233	2.088448
H	1.564573	-1.423604	2.731873	C	-0.298313	-2.690149	-3.660018
C	-4.549862	-1.324839	-0.381463	H	-0.276507	-3.602909	-4.2388
H	-5.356484	-1.286812	0.339259	C	-0.576017	-0.552241	-3.028862
C	1.380328	-2.553845	-2.207294	C	0.203739	-2.536174	-2.390657
C	-1.193384	4.64313	0.007199	C	0.318893	-2.687667	3.660062
H	-2.129063	5.191762	0.011914	H	0.30405	-3.600543	4.238879
C	-2.101275	-1.179232	3.821287	C	-4.889424	-1.795318	0.098282
H	-2.587201	-0.784081	4.702024	H	-5.942184	-2.05065	0.141514
C	-4.785173	-1.589651	-1.719729	C	0.580374	-0.547751	3.028796
H	-5.792978	-1.76408	-2.079036	C	-4.141053	-2.06866	-1.03223
C	2.191693	-2.497791	-3.311589	H	-4.579173	-2.542053	-1.901502
H	2.770341	-3.318284	-3.712185	C	-2.798544	-1.729066	-1.052367
C	0.767418	0.913664	-3.196255	H	-2.188367	-1.930479	-1.925006
H	-0.311695	0.958926	-3.381028	C	0.93767	0.89677	2.99508
H	1.264269	1.344547	-4.067013	H	1.731676	1.120759	2.276946
H	0.962606	1.555692	-2.336139	H	1.287046	1.199546	3.983843
C	-0.767514	0.91359	3.196231	H	0.090299	1.530142	2.724086
H	0.31162	0.958948	3.380849	C	-0.944124	0.889576	-2.995305
H	-1.264282	1.344392	4.067076	H	-1.739871	1.107734	-2.277304
H	-0.962886	1.555632	2.336169	H	-1.295628	1.189627	-3.984144
C	-3.250795	-1.109105	0.042358	H	-0.101544	1.529296	-2.724276
H	-3.026561	-0.910306	1.085038	C	0.80122	-1.420914	4.06711
C	4.54987	-1.324827	0.381424	H	1.253397	-1.166482	5.01524
H	5.356484	-1.286812	-0.339309	C	0.967656	-3.561265	-1.61994
C	2.998302	2.341995	1.486529	H	2.046101	-3.482881	-1.799176
H	3.209942	3.314606	1.94031	H	0.660174	-4.56091	-1.932523
H	3.909664	1.73806	1.54113	H	0.830404	-3.504979	-0.538843
H	2.225588	1.857315	2.086643	C	2.811625	-1.70801	1.052291
C	2.10137	-1.179057	-3.821255	H	2.202931	-1.914097	1.924858
H	2.587315	-0.783867	-4.701963	C	4.272268	-1.159509	-1.177181
C	3.2508	-1.109087	-0.042383	H	4.807197	-0.923942	-2.088325
H	3.026558	-0.910294	-1.085063	C	-1.219074	3.175865	0.174781
C	-1.380233	-2.553955	2.207273	C	-1.195335	4.563521	0.174222
C	-2.191556	-2.497961	3.311603	C	-0.020308	5.27157	0.000021
H	-2.770142	-3.31849	3.712212	C	1.160172	4.57265	-0.174177
C	3.709154	-1.627667	2.591611	C	1.19467	3.185211	-0.174766
H	3.841468	-1.830544	3.646566	H	-0.024514	6.355522	0.000031
C	4.785196	-1.589628	1.71969	H	2.086083	5.120943	-0.313227
H	5.793005	-1.76406	2.078986	H	-2.125472	5.104607	0.313303
C	-1.116429	-3.736446	1.344863	C	2.513928	2.483388	-0.388459
H	-1.331654	-3.553526	0.285416	C	3.608589	2.975744	0.554256
H	-1.75498	-4.564709	1.655722	H	3.876286	4.016953	0.356162
H	-0.080248	-4.084909	1.411328	H	3.296449	2.906086	1.59847
C	3.634921	3.158804	-0.801334	H	4.51538	2.377013	0.428585
H	3.307733	3.314995	-1.831685	C	2.96692	2.600581	-1.843298
H	4.519742	2.516164	-0.81963	H	3.135097	3.646635	-2.114673

H	3.949849	4.125115	-0.398423	H	2.217175	2.199715	-2.529596
C	-2.998219	2.341799	-1.486545	H	3.904915	2.060639	-2.005417
H	-3.209869	3.314383	-1.94038	H	2.341005	1.429476	-0.171329
H	-3.909545	1.737815	-1.541208	C	-2.532823	2.463777	0.388497
H	-2.225424	1.857139	-2.086569	C	-3.631305	2.947391	-0.554283
C	-3.635091	3.158652	0.80123	H	-3.318572	2.880121	-1.598478
H	-3.307995	3.314927	1.831598	H	-3.907269	3.986459	-0.356282
H	-4.519861	2.515942	0.819493	H	-4.533336	2.341506	-0.428616
H	-3.950068	4.124913	0.39824	C	-2.986712	2.577554	1.84334
C	1.116548	-3.736357	-1.344905	H	-3.162997	3.622305	2.114595
H	1.33177	-3.553456	-0.285453	H	-3.920489	2.030368	2.005519
H	1.755117	-4.564601	-1.655781	H	-2.233873	2.182605	2.529685
H	0.080375	-4.084839	-1.41138	H	-2.351621	1.411243	0.171476

XRD Crystallography

For single crystal X-ray diffraction analysis, suitable crystals were placed onto MiTeGen loop pins coated in Paratone[®] oil and mounted under a flow of nitrogen at 100 K on a Bruker Smart Apex II diffractometer with CCD area detector using Mo K α irradiation. Using Olex2^[9] the structures were solved with the SUPERFLIP package^[10, 11] and refined using SHELXL^[12]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in ideal positions and refined as riding atoms.

Table S12. Crystal data, data collection and structure refinement parameters for compounds **1a**, **1b**.

Identification code	1a	1b
CCDC Deposition Number	2158160	2158161
Empirical formula	C ₂₆ H ₃₅ N ₅ Zr	C ₃₄ H ₄₃ N ₅ Zr
Formula weight	508.81	612.95
Temperature/K	100.01	100.0
Crystal system	triclinic	monoclinic
Space group	P -1	P2 ₁ /c
a/Å	9.5458(3)	14.7788(3)
b/Å	10.0123(3)	11.6370(2)
c/Å	14.9998(5)	19.7916(4)
α /°	101.922(2)	90
β /°	92.277(2)	109.9450(10)
γ /°	111.033(2)	90
Volume/Å ³	1299.01(7)	3199.62(11)
Z	2	4
ρ_{calc} /g/cm ³	1.301	1.272
μ /mm ⁻¹	0.445	0.373
F(000)	532.0	1288.0
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 θ range for data collection/°	4.486 to 52.742	4.128 to 52.804
Index ranges	-10 \leq h \leq 11, -12 \leq k \leq 12, -16 \leq l \leq 18	-18 \leq h \leq 18, -14 \leq k \leq 14, -24 \leq l \leq 24
Reflections collected	29762	47298
Independent reflections	5273 [R _{int} = 0.0433, R _{sigma} = 0.0359]	6572 [R _{int} = 0.0380, R _{sigma} = 0.0255]
Data/restraints/parameters	5273/0/296	6572/0/369
Goodness-of-fit on F ²	1.040	1.047
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0404, wR ₂ = 0.0983	R ₁ = 0.0308, wR ₂ = 0.0783
Final R indexes [all data]	R ₁ = 0.0495, wR ₂ = 0.1043	R ₁ = 0.0394, wR ₂ = 0.0823
Largest diff. peak/hole / e Å ⁻³	0.95/-0.52	0.58/-0.39

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