Supporting Information

Manuscript Title:

Reaction of Titanacyclobutene-Silacyclobutene Fused-Ring Complexes with Nitriles *via* Formal Insertion of the C-N Triple Bond of Nitrile into the Silacyclobutene Ring

Authors:

Jing Zhao,[†] Shaoguang Zhang,[‡] Wen-Xiong Zhang,*[,‡] and Zhenfeng Xi*[,‡,§]

Affiliations:

[†] Beijing National Laboratory of Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing 100190, China;

[‡] Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China;

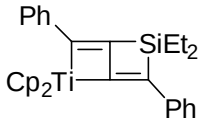
[§] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

E-mail: wx_zhang@pku.edu.cn; zfxi@pku.edu.cn

Contents:

1) Experimental details and characterization data for 5b and 6a-e.

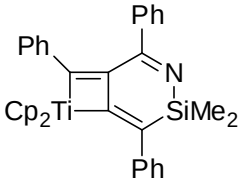
General Procedures. All reactions were carried out under a slightly positive pressure of dry and oxygen-free nitrogen by using standard Schlenk line techniques or under a nitrogen atmosphere in a glovebox. The nitrogen in the glovebox was constantly circulated through a copper/molecular sieves catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored to ensure both were always below 1 ppm. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Solvent was distilled from sodium/benzophenone under a nitrogen atmosphere. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker-400 spectrometer (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C) and a Bruker-500 spectrometer (FT, 500 MHz for ^{1}H; 125 MHz for ^{13}C) at room temperature. Organometallic samples for NMR spectroscopic measurements were prepared in the glovebox by use of J. Young valve NMR tubes (Wilmad 528-JY).



5b

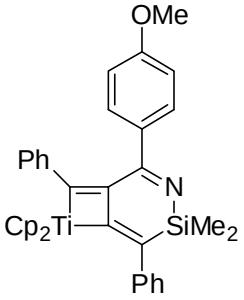
Isolation of Complex 5b. In a 20 mL Schlenk tube, $Et_2Si(C{\equiv}CPh)_2$ (288 mg, 1.0 mmol) was added to the solution of [Ti(η^5-C_5H_5)$_2$(η^2-btmse)] (348 mg, 1.0 mmol) in benzene and the resulting mixture was heated to 80 ^{o}C for 3 h.[1] All volatiles were distilled off at 80 ^{o}C in vacuum to give red solids **5b** (354 mg, 76% based on 1 mmol scale). ^{1}H NMR (500 MHz, C_6D_6): δ = 0.89-0.92 (m, 10H, $SiEt_2$), 5.32 (s, 10H, C_5H_5), 7.18-7.23 (m, 2H, C_6H_5), 7.37-7.45 (m, 4H, C_6H_5), 7.65 (d, J = 7.5 Hz, 2H, C_6H_5), 7.89 (d, J = 7.0 Hz, 2H, C_6H_5); ^{13}C NMR (125 MHz, C_6D_6): δ = 7.75 (s, 2 CH_2), 7.97 (s, 2 CH_3), 76.16 (s, 1 quat. C), 105.95 (s, 10 CH), 127.09 (s, 1 CH), 127.23 (s, 2 CH), 127.80 (s, 1 CH), 128.85 (s, 2 C), 129.10 (s, 2 CH), 129.73 (s, 2 CH), 141.14 (s, 1 quat. C), 141.31 (s, 1 quat. C), 152.19 (s, 1 quat. C), 212.10 (s, 1 quat. C), 261.62 (s, 1 quat. C).

Formation of complexes 6a-c from complex 5a and arylnitriles. A general procedure for preparation of 6a: In a 20 mL Schlenk tube, PhCN (75 μL, 0.75 mmol) was added to the benzene solution (5 mL) of compound **5a** (219 mg, 0.5 mmol). After the reaction mixture was stirred at 80 ^{o}C for 5 h, it was dried up under vacuum and the residue was washed with hexane. After filtering, the solid was dried up under vacuum to precipitate **6a** as dark green solids.



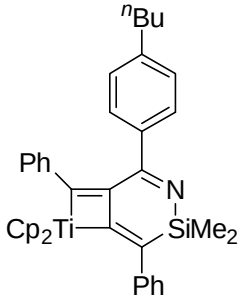
6a

Dark green solid, 181 mg, 67% based on 0.5 mmol scale. ^{1}H NMR (400 MHz, C_6D_6): δ = 0.66 (s, 6H, $SiMe_2$), 5.73 (s, 10H, C_5H_5), 6.61 (d, J = 7.2 Hz, 2H, C_6H_5), 6.71 (t, J = 7.5 Hz, 1H, C_6H_5), 6.84-7.25 (m, 10H, C_6H_5), 7.70 (d, J = 6.8 Hz, 2H, C_6H_5); ^{13}C NMR (100 MHz, C_6D_6): δ = 0.57 (s, 2 CH_3), 95.69 (s, 1 quat. C), 113.26 (s, 10 CH), 125.53 (s, 1 CH), 125.76 (s, 1 CH), 126.78 (s, 2 CH), 127.18 (s, 2 CH), 127.48 (s, 2 CH), 127.83 (s, 2 CH), 128.24 (s, 2 CH), 128.47 (s, 1 CH), 129.09 (s, 2 CH), 141.60 (s, 1 quat. C), 144.60 (s, 1 quat. C), 145.56 (s, 1 quat. C), 147.75 (s, 1 quat. C), 174.12 (s, 1 quat. C), 214.26 (s, 1 quat. C), 214.85 (s, 1 quat. C). Single crystals of **6a** suitable for X-ray analysis were grown in THF at room temperature. Elemental Analysis Calcd (%) for $C_{35}H_{31}NSiTi$: C, 77.62; H, 5.77; N, 2.59; Found: C, 77.24; H, 5.91; N, 2.28.



6b

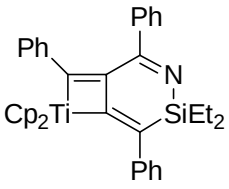
Dark green solid, 180 mg, 63% based on 0.5 mmol scale. ^{1}H NMR (400 MHz, C_6D_6): δ = 0.67 (s, 6H, $SiMe_2$), 3.15 (s, 3H, OCH_3), 5.75 (s, 10H, C_5H_5), 6.58 (d, J = 7.6 Hz, 2H, Ar), 6.67-7.26 (m, 10H, Ar), 7.76 (d, J = 7.6 Hz, 2H, Ar); ^{13}C NMR (100 MHz, C_6D_6): δ = 0.65 (s, 2 CH_3), 54.59 (s, 1 CH_3), 95.83 (s, 1 quat. C), 112.67 (s, 2 CH), 113.23 (s, 10 CH), 125.51 (s, 1 CH), 125.83 (s, 1 CH), 127.09 (s, 2 CH), 127.48 (s, 2 C), 127.89 (s, 2 CH), 128.23(s, 2 CH), 130.77 (s, 2 CH), 137.05 (s, 1 quat. C), 141.77 (s, 1 quat. C), 145.50 (s, 1 quat. C), 147.84 (s, 1 quat. C), 160.48 (s, 1 quat. C), 173.49 (s, 1 quat. C), 213.83 (s, 1 quat. C), 214.87 (s, 1 quat. C).



6c

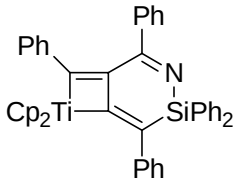
Dark green solid, 212 mg, 71% based on 0.5 mmol scale. ^{1}H NMR (500 MHz, C_6D_6): δ = 0.66 (s, 6H, $SiMe_2$), 0.85 (t, J = 7.5 Hz, 3H, $CH_3CH_2CH_2CH_2$), 1.09-1.61 (m, 2H, $CH_3CH_2CH_2CH_2$), 1.35-1.41 (m, 2H, $CH_3CH_2CH_2CH_2$), 2.32 (t, J = 7.5 Hz, 2H, $CH_3CH_2CH_2CH_2$), 5.75 (s, 10H, C_5H_5), 6.64 (d, J = 7.5 Hz, 2H, Ar), 6.73 (t, J = 7.5 Hz, 1H, C_6H_5), 6.81 (d, J = 8.0 Hz, 2H, Ar), 6.85-7.25 (m, 7H, Ar), 7.66 (d, J = 8.0 Hz, 2H, Ar); ^{13}C NMR (125 MHz, C_6D_6): δ = 0.60 (s, 2 CH_3), 14.12 (s, 1 CH_3), 22.21 (s, 1 CH_2), 33.62 (s, 1 CH_2), 35.53 (s, 1 CH_2), 95.53 (s, 1 quat. C), 113.22 (s, 10 CH), 125.51 (s, 1 CH), 125.59 (s, 1 CH), 126.90 (s, 2 CH), 127.36 (s, 2 C), 127.50 (s, 2 CH), 127.77(s, 2 CH), 128.22 (s, 2 CH), 129.19 (s, 2 CH), 141.74 (s, 1 quat. C), 142.21 (s, 1 quat. C), 142.97 (s, 1 quat. C), 145.65 (s, 1 quat. C), 147.82 (s, 1 quat. C), 174.16 (s, 1 quat. C), 214.69 (s, 1 quat. C), 214.71 (s, 1 quat. C).

Formation of complexes 6d,e from complexes 5b,c and PhCN. A general procedure for preparation of 6d: In a 20 mL Schlenk tube, PhCN (75 μL, 0.75 mmol) was added to the benzene solution (5 mL) of compound **5b** (233 mg, 0.5 mmol). After the reaction mixture was stirred at 80 ^{o}C for 21 h, it was dried up under vacuum and the residue was washed with hexane. After filtering, the solid was dried up under vacuum to precipitate **6d** as dark green solids.



6d

Dark green solid, 188 mg, 66% based on 0.5 mmol scale. ^{1}H NMR (400 MHz, C_6D_6): δ = 1.03-1.21 (m, 10H, $SiEt_2$), 5.77 (s, 10H, C_5H_5), 6.61 (d, J = 7.2 Hz, 2H, C_6H_5), 6.71 (t, J = 7.0 Hz, 1H, C_6H_5), 6.85-6.97 (m, 6H, C_6H_5), 7.12-7.24 (m, 4H, C_6H_5), 7.66 (d, J = 6.8 Hz, 2H, C_6H_5); ^{13}C NMR (100 MHz, C_6D_6): δ = 7.92 (s, 2 CH_3 & 2 CH_2), 96.23 (s, 1 quat. C), 113.30 (s, 10 CH), 125.45 (s, 1 CH), 125.63 (s, 1 CH), 126.74 (s, 2 CH), 127.17 (s, 2 C), 127.38 (s, 2 CH), 127.81 (s, 2 CH), 128.22 (s, 2 CH), 128.33 (s, 1 CH), 129.10 (s, 2 CH), 139.19 (s, 1 quat. C), 144.87 (s, 1 quat. C), 145.67 (s, 1 quat. C), 148.14 (s, 1 quat. C), 174.79 (s, 1 quat. C), 214.46 (s, 1 quat. C), 215.60 (s, 1 quat. C). Single crystals of **6d** suitable for X-ray analysis were grown in THF at room temperature. Elemental Analysis Calcd (%) for $C_{37}H_{35}NSiTi$: C, 78.01; H, 6.19; N, 2.46; Found: C, 77.90; H, 6.21; N, 2.37.



6e

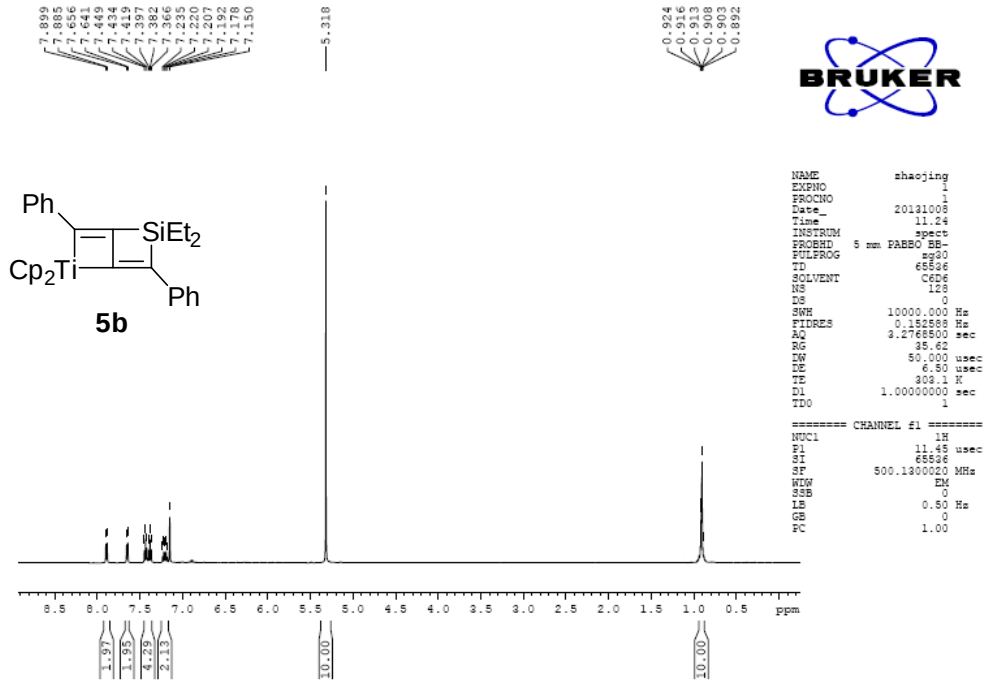
Dark green solid, 263 mg, 79% based on 0.5 mmol scale. ^{1}H NMR (400 MHz, C_6D_6): 5.75 (s, 10H, C_5H_5), 6.65 (d, J = 7.2 Hz, 2H, C_6H_5), 6.72 (t, J = 7.2 Hz, 1H, C_6H_5), 6.84-7.10 (m, 13H, C_6H_5), 7.18-7.37 (m, 3H, C_6H_5), 7.72 (d, J = 7.2 Hz, 2H, C_6H_5), 8.05-8.13 (m, 4H, C_6H_5); ^{13}C NMR data were not collected because of the poor solubility of **6e** in C_6D_6, THF-d_8, toluene-d_8, etc. Single crystals of **6e** suitable for X-ray analysis were grown in THF at room temperature. Elemental Analysis Calcd (%) for $C_{45}H_{35}NSiTi$: C, 81.19; H, 5.30; N, 2.10; Found: C, 80.82; H, 5.47; N, 1.99.

Reference:

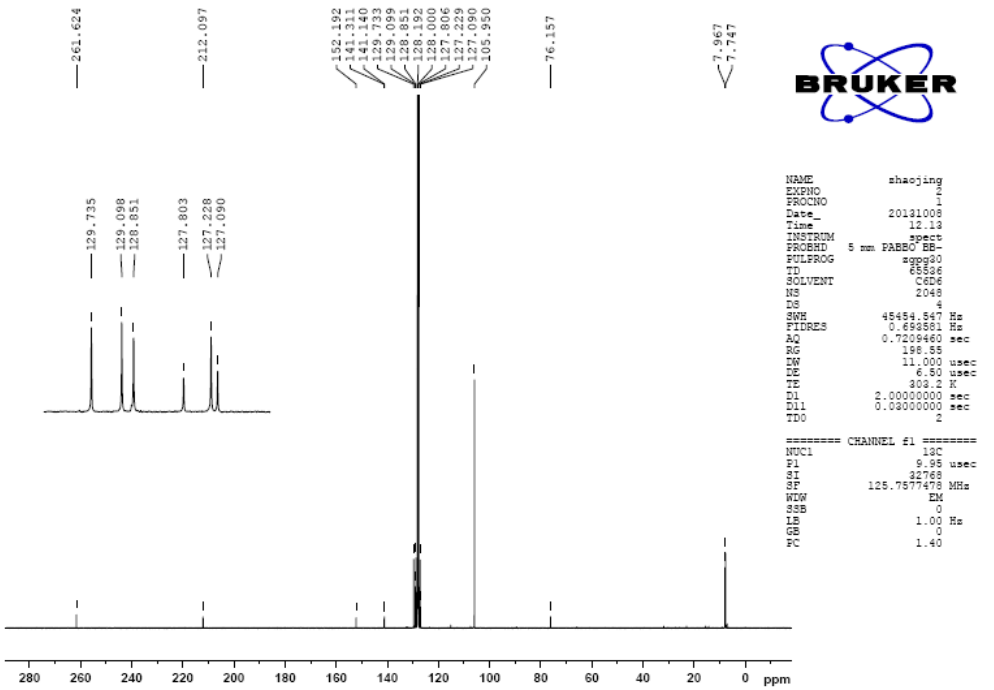
1. Horáček, M.; Bazyakina, N.; Štepnička, P.; Gyepes, R.; Císařová, I.; Bredeau, S.; Meunier, P.; Kubišta, J.; Mach, K. *J. Organomet. Chem.* **2001**, *628,* 30-38.

2) ^{1}H NMR and ^{13}C NMR Spectra of All New Compounds

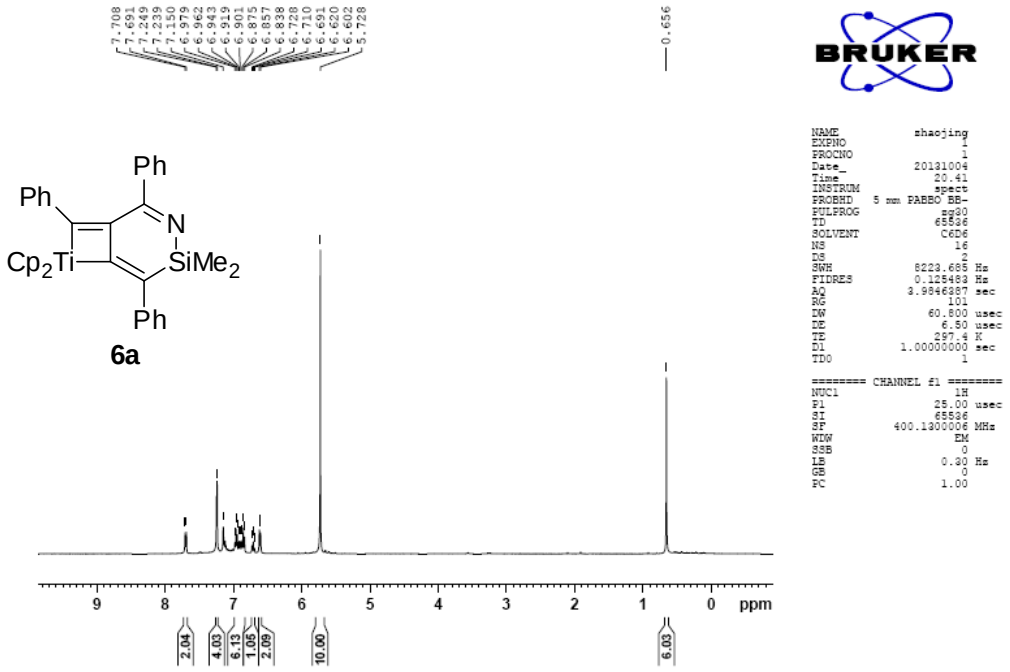
^{1}H NMR-**5b**



^{13}C NMR-**5b**



^{1}H NMR-**6a**

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FIDRES             0.125483 Hz
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DE                   6.50 usec
TE                   297.4 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
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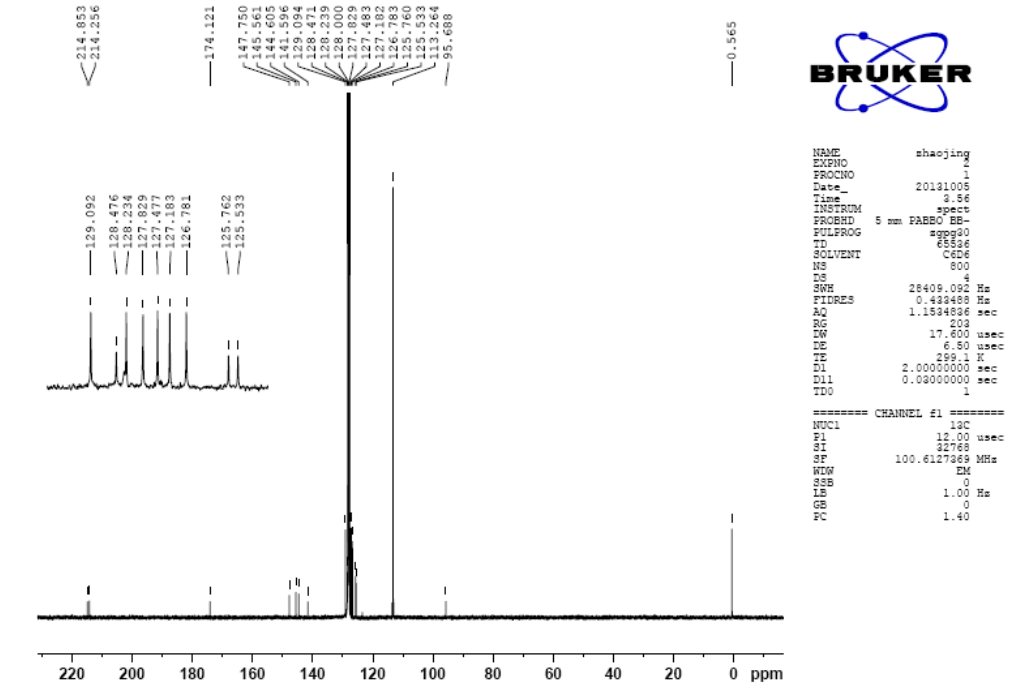
^{13}C NMR-**6a**

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TD0                        1

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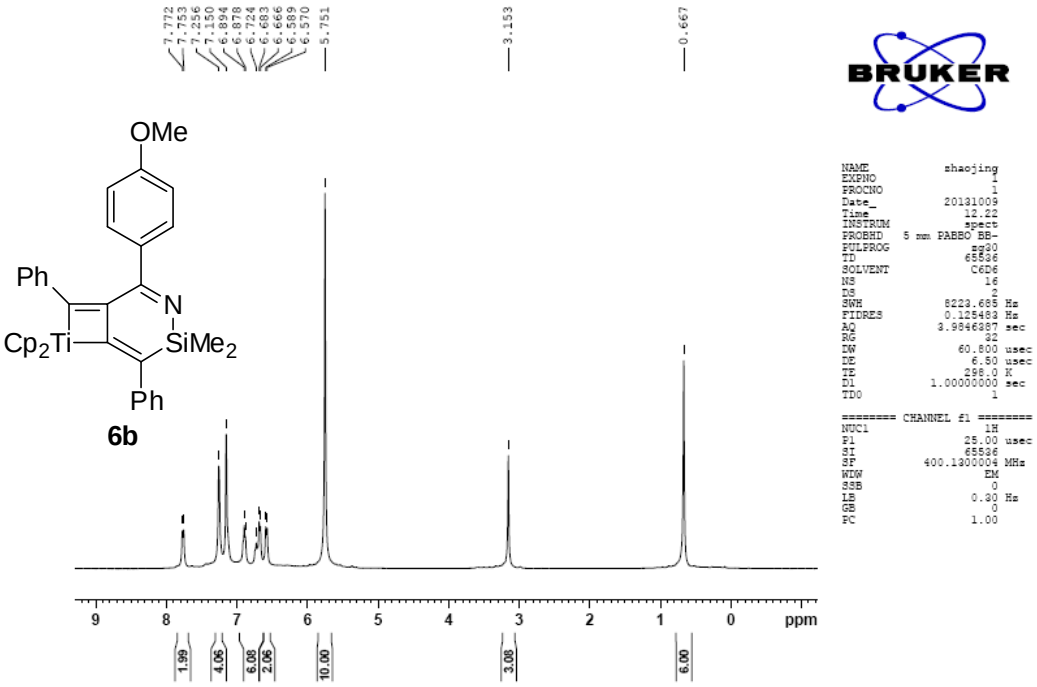
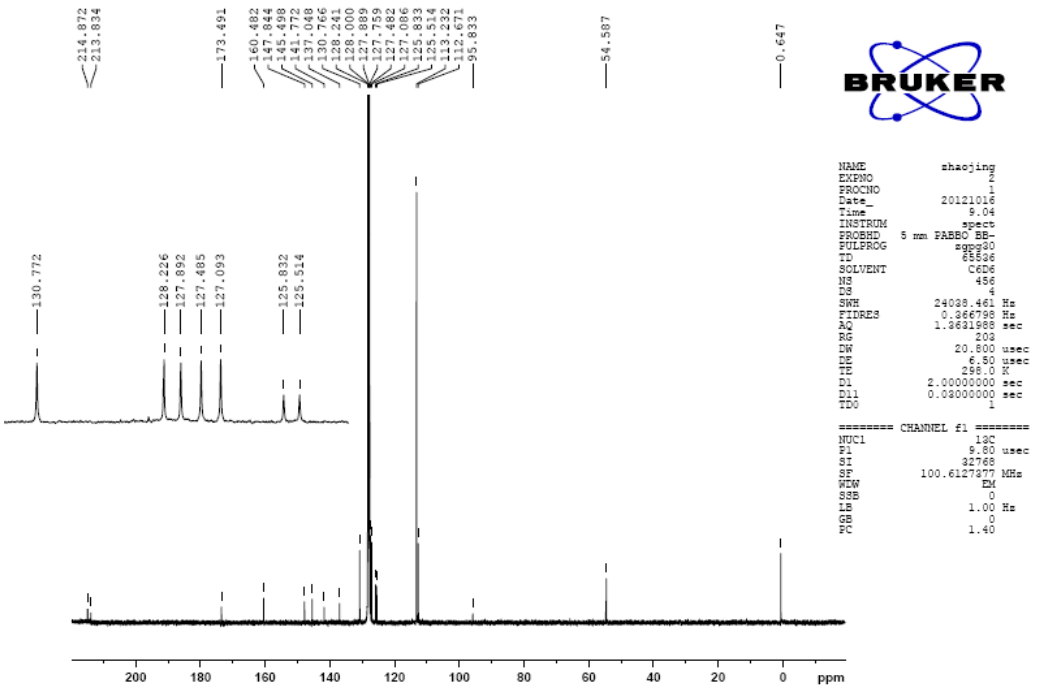
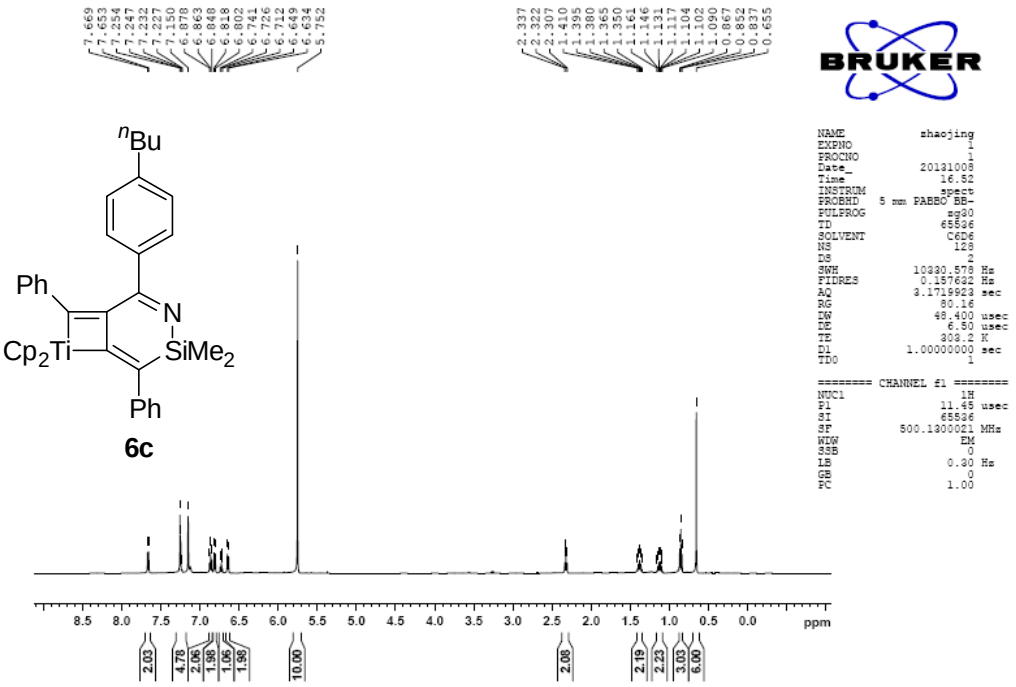
^{1}H NMR-**6b**



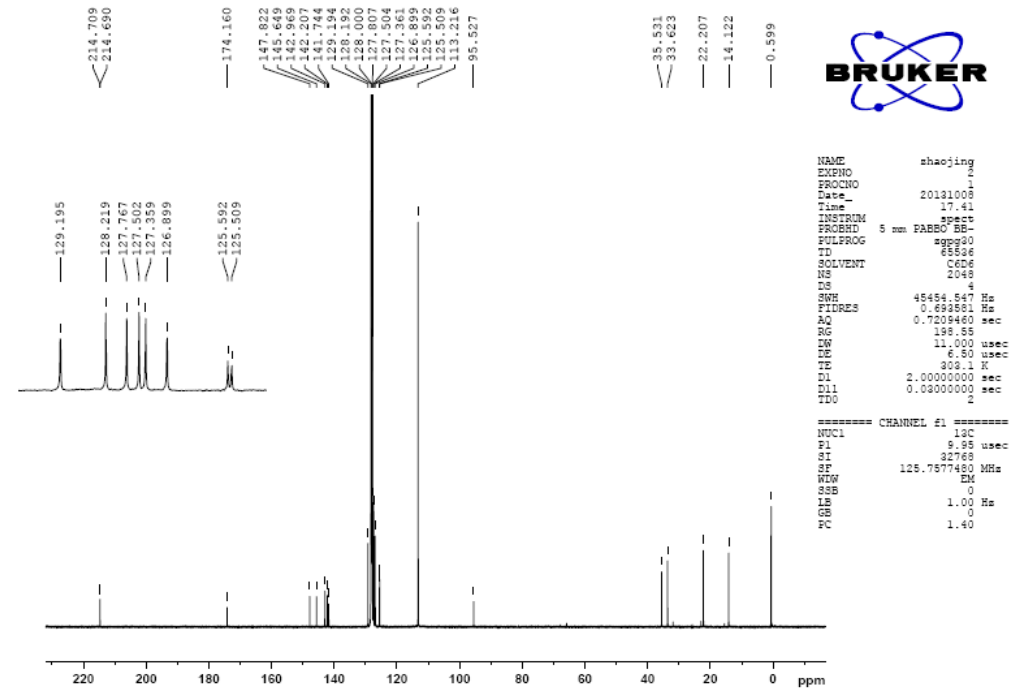
^{13}C NMR -**6b**



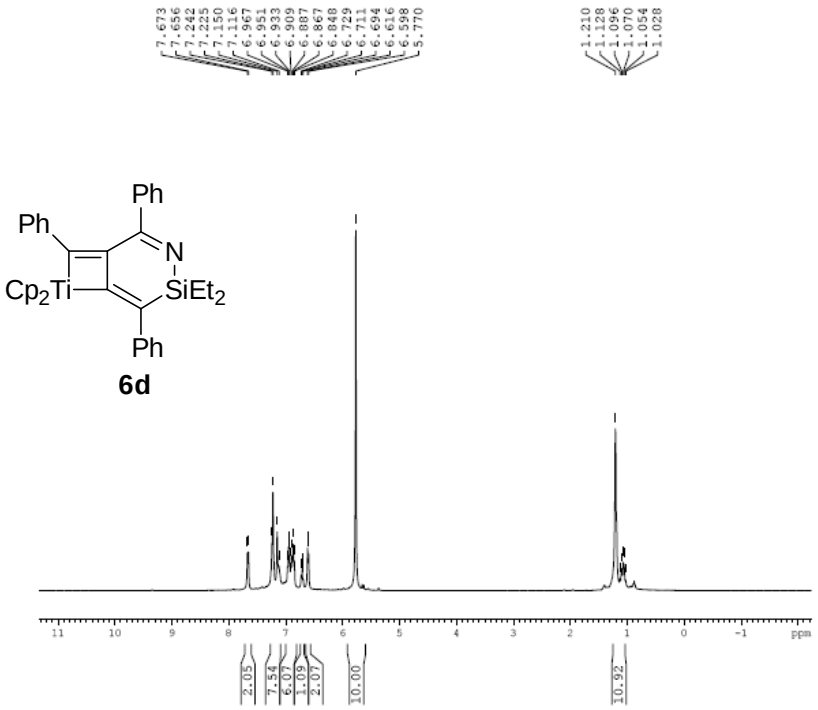
^{1}H NMR-**6c**



^{13}C NMR-**6c**



^{1}H NMR-**6d**

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TD                      65536
SOLVENT                  C6D6
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FIDRES             0.125483 Hz
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TE                    297.4 K
D1                 1.00000000 sec
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======== CHANNEL f1 ========
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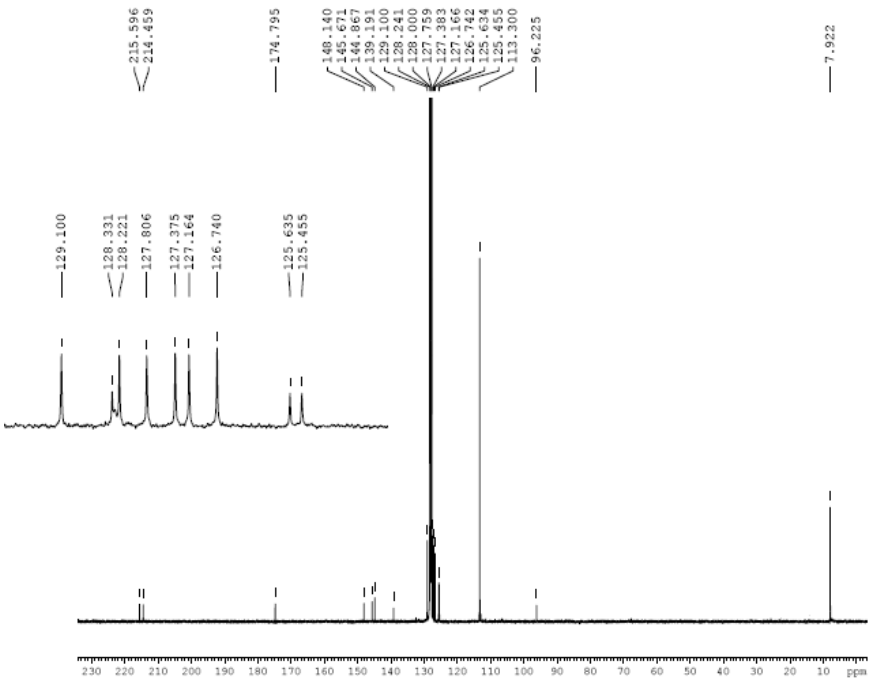
^{13}C NMR-**6d**

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FIDRES             0.433488 Hz
AQ                 1.1534826 sec
RG                       203
DW                    17.600 usec
DE                     6.50 usec
TE                    299.1 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                          1

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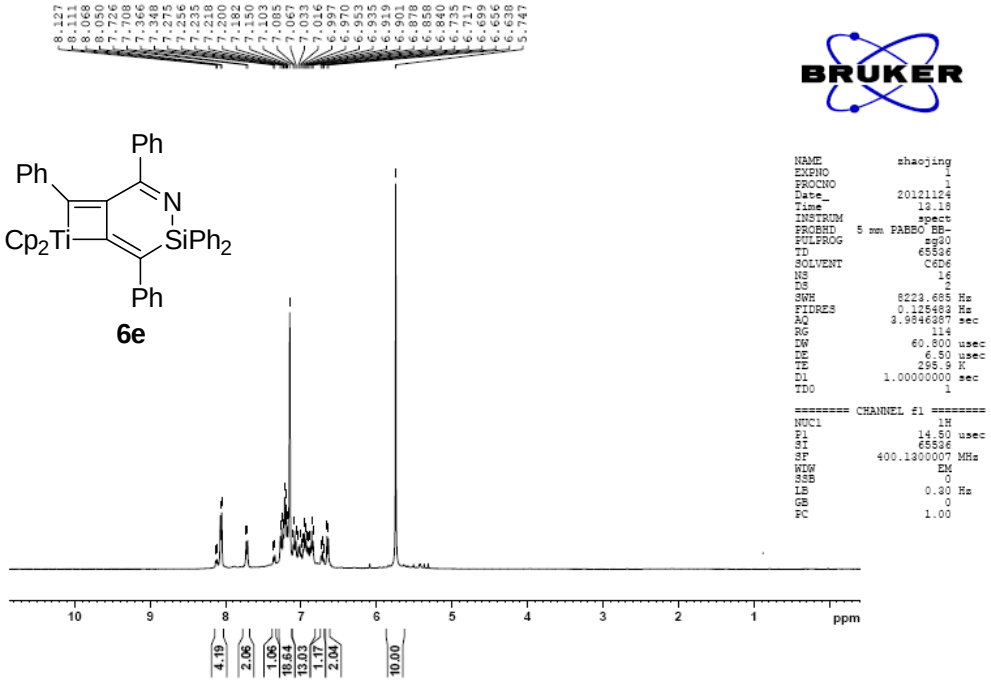
^{1}H NMR-**6e**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FIDRES 0.125483 Hz
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TE 295.9 K
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8
7
6
5
4
3
2
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ppm
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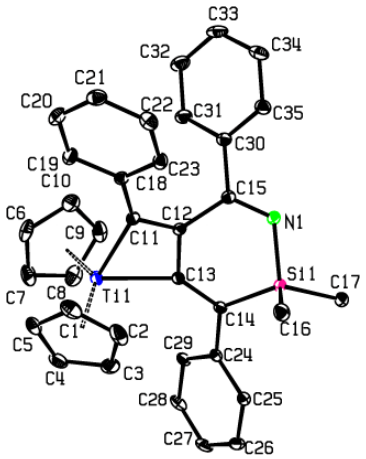
2.06
1.06
16.64
13.03
1.17
2.04
10.00

3) X-ray crystallographic studies

Crystals for X-ray analysis of **6a**, **6d** and **6e** were obtained as described in the preparations. Data collections for **6a**, **6d** and **6e** were performed at 100K, 180 K and 180K on a SuperNova diffractometer using graphite-monochromated Mo Kα radiation (λ= 0.71073 Å). Using Olex2, the structure of **6a**, **6d** and **6e** were solved with the Superflip structure solution program using Charge Flipping and refined with the XL refinement package using Least Squares minimisation. Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-966743 (**6a**), CCDC-966742 (**6d**), and CCDC-966744 (**6e**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

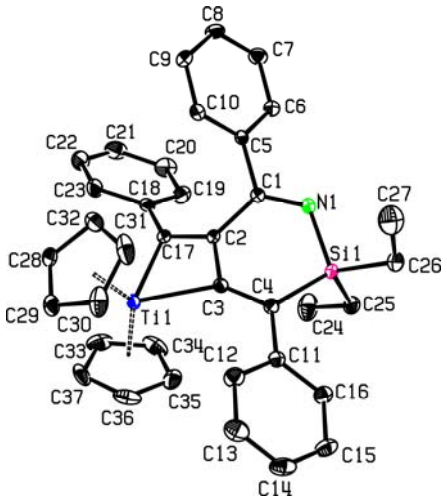


SFigure 1. ORTEP drawing of **6a** with 30% thermal ellipsoids. Hydrogen atoms have been omitted.

STable 1. Crystal data and structure refinement for **6a**.

Identification code	**6a**
Empirical formula	$C_{35}H_{31}NSiTi$
Formula weight	541.60
Temperature	99.98(11) K
Crystal system, space group	Monoclinic, *P*21/c
Unit cell dimensions	a = 15.9762(8) Å alpha = 90.00°
	b = 11.2754(4) Å beta = 115.916(6)°
	c = 17.1936(9) Å gamma = 90°
Volume	2785.8(2) $Å^3$
Z, Density (calculated)	4, 1.291 Mg/m^3

Absorption coefficient	0.375 mm^-1
F(000)	1136.0
Crystal size	0.20 × 0.20 × 0.10 mm^3
Theta range for data collection	5.82 to 52.04°
Index ranges	-18 ≤ h ≤ 19, -13 ≤ k ≤ 13, -21 ≤ l ≤ 15
Reflections collected / Independent reflections	25221 / 5487[R(int) = 0.0490]
Data / restraints / parameters	5487/0/345
Goodness-of-fit on F^2	1.044
Final R indices [I>2sigma(I)]	R1 = 0.0389, wR2 = 0.0945
R indices (all data)	R1 = 0.0489, wR2 = 0.1020
Largest diff. peak and hole	0.40/-0.41 e. $Å^{-3}$

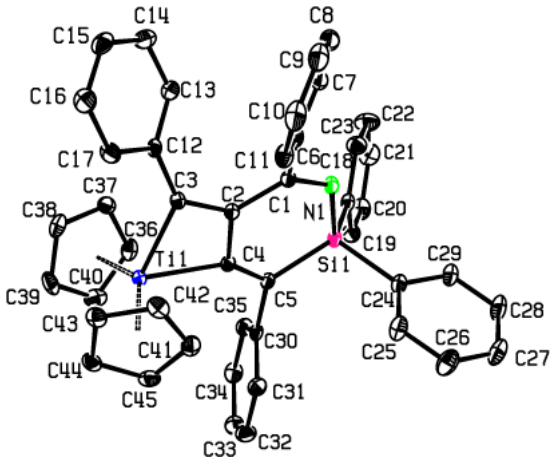


SFigure 2. ORTEP drawing of **6d** with 30% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

STable 2. Crystal data and structure refinement for **6d**.

Identification code	**6d**
Empirical formula	$C_{37}H_{35}NSiTi$
Formula weight	569.65
Temperature	180.15 K
Crystal system, space group	Monoclinic, $P2_1/n$
Unit cell dimensions	a = 10.2052(3) Å alpha = 90°

	b = 17.3311(5) Å beta = 99.069(3)°
	c = 17.0297(6) Å gamma = 90°
Volume	2974.35(17) $Å^3$
Z, Calculated density	4, 1.272 Mg/m^3
Absorption coefficient	0.355 mm^-1
F(000)	1200.0
Crystal size	0.2 × 0.1 × 0.1 mm^3
Theta range for data collection	6.2 to 50.054°
Limiting indices	-8 ≤ h ≤ 12, -20 ≤ k ≤ 17, -18 ≤ l ≤ 20
Reflections collected / unique	11341 / 5222[R(int) = 0.0223]
Data / restraints / parameters	5222/0/363
Goodness-of-fit on F^2	1.051
Final R indices [I>2sigma(I)]	R1 = 0.0386, wR2 = 0.0935
R indices (all data)	R1 = 0.0478, wR2 = 0.1000
Largest diff. peak and hole	0.60 and -0.39 e. $Å^{-3}$



SFigure 3. ORTEP drawing of **6e** with 30% thermal ellipsoids. Hydrogen atoms and THF have been omitted for clarity.

STable 3. Crystal data and structure refinement for **6e**.

Identification code	**6e**
Empirical formula	$C_{49}H_{43}NSiTiO$
Formula weight	737.83
Temperature	180.15 K

Crystal system, space group	Monoclinic, *C*2/c
Unit cell dimensions	a = 16.2653(6) Å alpha = 90°
	b = 19.3916(6) Å beta = 104.915(3)°
	c = 24.7760(8) Å gamma = 90°
Volume	7551.3(4) $Å^3$
Z, Calculated density	8, 1.298 Mg/m^3
Absorption coefficient	0.298 mm^-1
F(000)	3104.0
Crystal size	0.20 x 0.10 x 0.10 mm^3
Theta range for data collection	6.55 to 52.038°
Limiting indices	-20 ≤ h ≤ 17, -19 ≤ k ≤ 23, -30 ≤ l ≤ 24
Reflections collected / unique	14417 / 7392[R(int) = 0.0218]
Data / restraints / parameters	7392/4/487
Goodness-of-fit on F^2	1.036
Final R indices [I>2sigma(I)]	R1 = 0.0469, wR2 = 0.1209
R indices (all data)	R1 = 0.0576, wR2 = 0.1291
Largest diff. peak and hole	0.69 and -0.48 e. $Å^{-3}$