Supporting Information

Synthesis, structure and DFT calculations of a mononuclear cyclic (alkyl)(amino) carbene supported Titanium(II) complex

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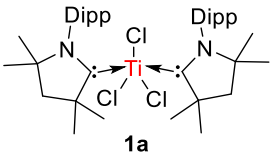
Experimental details

Unless otherwise noted, all reactions were conducted under slightly positive dry nitrogen or argon pressure using standard Schlenk line techniques or under a nitrogen atmosphere in a Vigor (SG 2400/750TS-F) glovebox. The nitrogen in the glove box was constantly circulated through a copper/molecular sieves catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O Combi-Analyzer to ensure both were always below 1 ppm. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Solvents were purified by Vigor (VSPS-5) Solvent Purification System and dried over fresh Na chips in a glovebox. Organometallic samples for NMR spectroscopic measurements were prepared in a glovebox by the use of J.Young valve NMR tubes (Wilmad 528-JY). Compounds mer-$[TiCl_3(THF)_3]$,[1] cAAC[2] and KC_8[3] were prepared following literature procedures. ^1H, and ^{13}C NMR spectra were recorded on a Bruker AVANCE NEO 400 spectrometer (FT, 400 MHz for ^1H; 100 MHz for ^{13}C) at room temperature, unless otherwise noted. Elemental analyses were performed on a Vario EL cube elemental analyzer. The EPR spectrum was recorded with a Bruker ELEXYS E500 spectrometer.

Synthesis of **1a**: In a glovebox, $TiCl_3(THF)_3$ (370.5 mg, 1.0 mmol) was dissolved in THF (~10 mL) in a 50 mL flask. A THF (~10 mL) solution of two equiv. of free cAAC (571.0 mg, 2.0 mmol) was added dropwise into the suspension. The obtained mixture was stirred at room temperature for 2 h. All volatiles were removed under reduced pressure and the crude product was obtained as a purple solid. Single crystals of **1a** suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane into an Et_2O solution of **1a** at –30 ºC for one day.



1a

1a: Purple solid, isolated yield 90% (652.5 mg). $C_{40}H_{62}Cl_3N_2Ti$: C, 66.25; H, 8.62; N, 3.86; found C 65.10; H, 8.83; N, 3.84 %. **EPR** (Toluene, 298 K): g = 1.97.

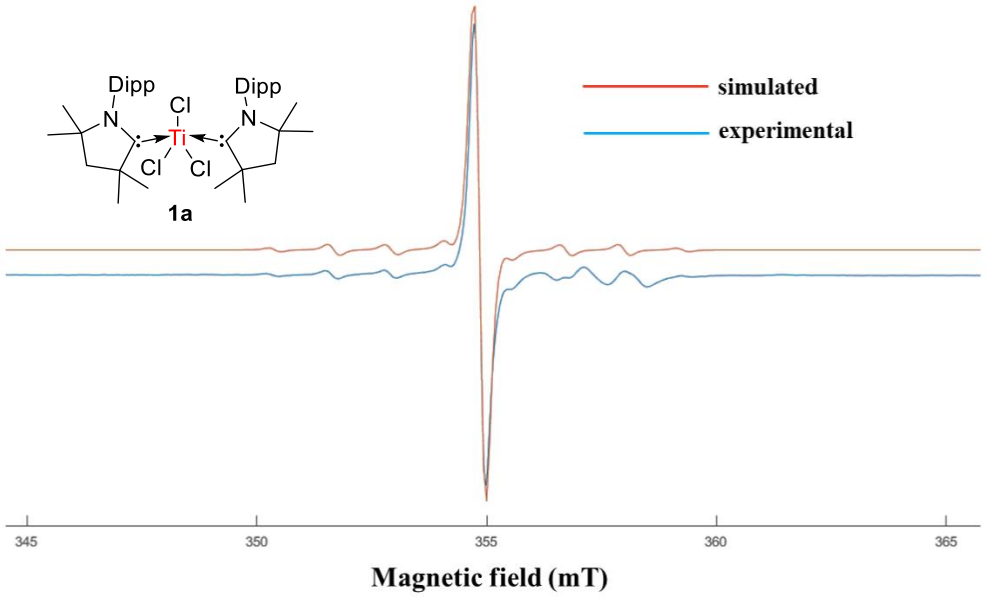
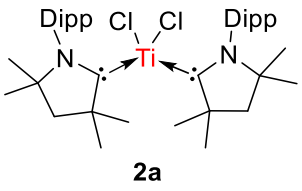


Figure S1. Experimental X-band (9.6 GHz) EPR spectrum of **1a** (blue) in toluene solution at 298 K. In the simulation (red), the ^{14}N, ^{47}Ti and ^{49}Ti hyperfine interactions are considered.

Synthesis of **2a**: In a glovebox, KC_8 (20.3 mg, 0.15 mmol) was added to a toluene (~10 mL) solution of complex **1a** (72.5 mg, 0.1 mmol) in a 25 mL flask. The obtained reaction mixture was stirred at room temperature for 24 h. KCl and graphite were removed by filtration. The filtrate was concentrated to about 2 mL and was stored at –30 ºC for one day to get compound **2a** as a black crystalline solid. Single crystals of **2a** suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a toluene solution of **2a** at –30 ºC for one week.



2a

2a: Black solid, isolated yield 35% (24.1 mg). ^{1}H NMR (400 MHz, Tol-d_8, 0 ºC) δ (ppm) 0.80 (s, 6H), 1.06 (d, *J* = 6.6 Hz, 6H), 1.29 (d, *J* = 6.6 Hz, 6H), 1.33 (s, 6H), 1.37-1.38 (m, 8H), 1.42-1.46 (m, 8H), 1.61 (s, 6H), 1.76 (d, *J* = 6.6 Hz, 6H), 2.53 (sept, 2H), 3.77 (sept, 2H), 7.15-7.17 (m, 2H), 7.26-7.32 (m, 4H). ^{13}C NMR (100 MHz, Tol-d_8, 0 ºC) δ (ppm) 148.80, 146.87, 140.79, 128.63, 126.43, 124.94, 74.81, 55.08, 50.28, 35.96, 33.95, 31.43, 29.22, 27.64, 27.59, 27.38, 26.86, 25.20. (Some of ^{13}C signals are overlapped with Tol-d_8 solvent signal and the carbene C atom of cAAC could not be detected even after 2000 times of scan.) $C_{40}H_{62}Cl_2N_2Ti$: C, 69.66; H, 9.06; N, 4.06; found C 68.94; H, 9.07; N, 4.16 %.

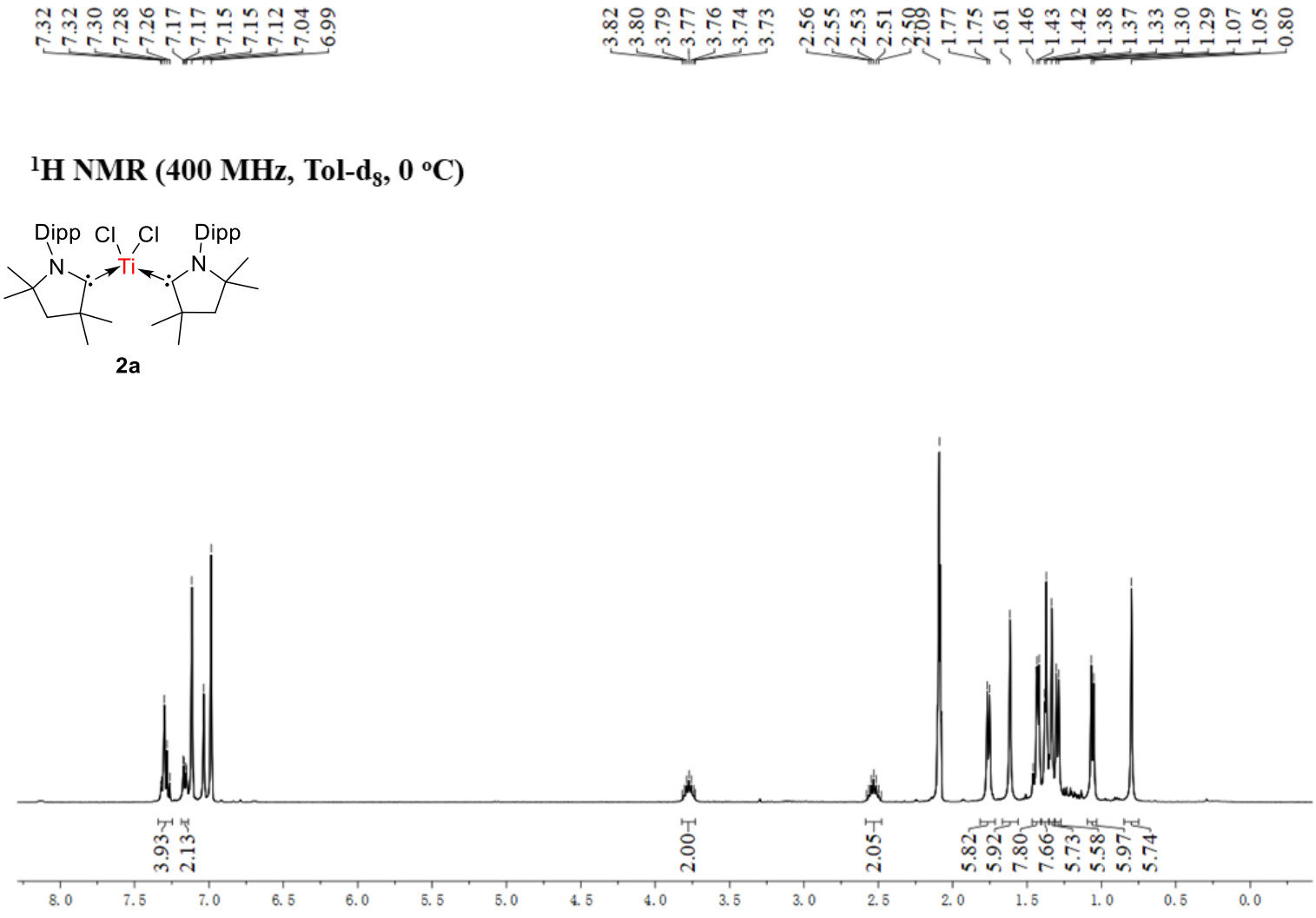


Fig. S2. ^{1}H NMR spectrum of **2a**.

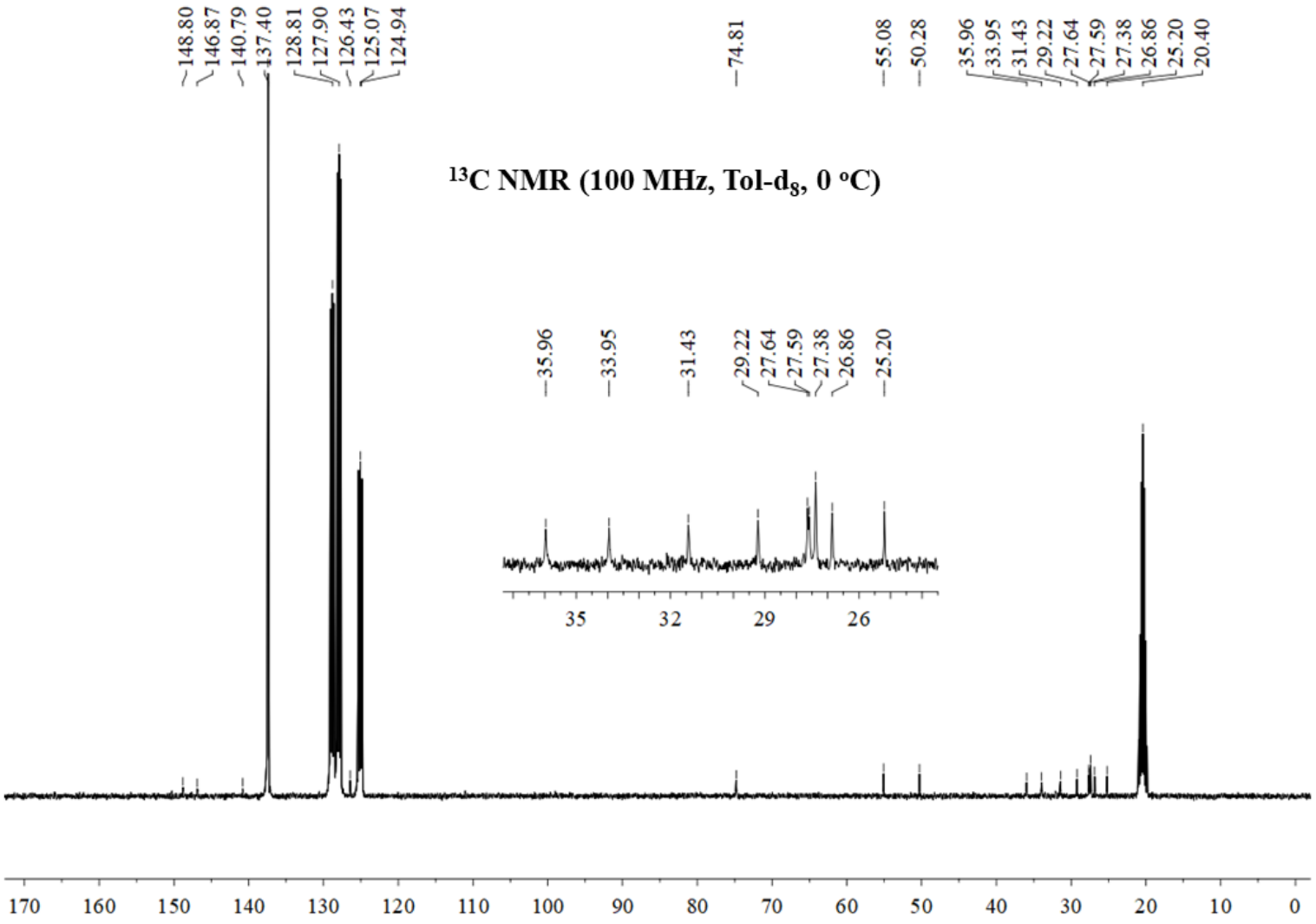


Fig. S3. ^{13}C NMR spectrum of **2a**.

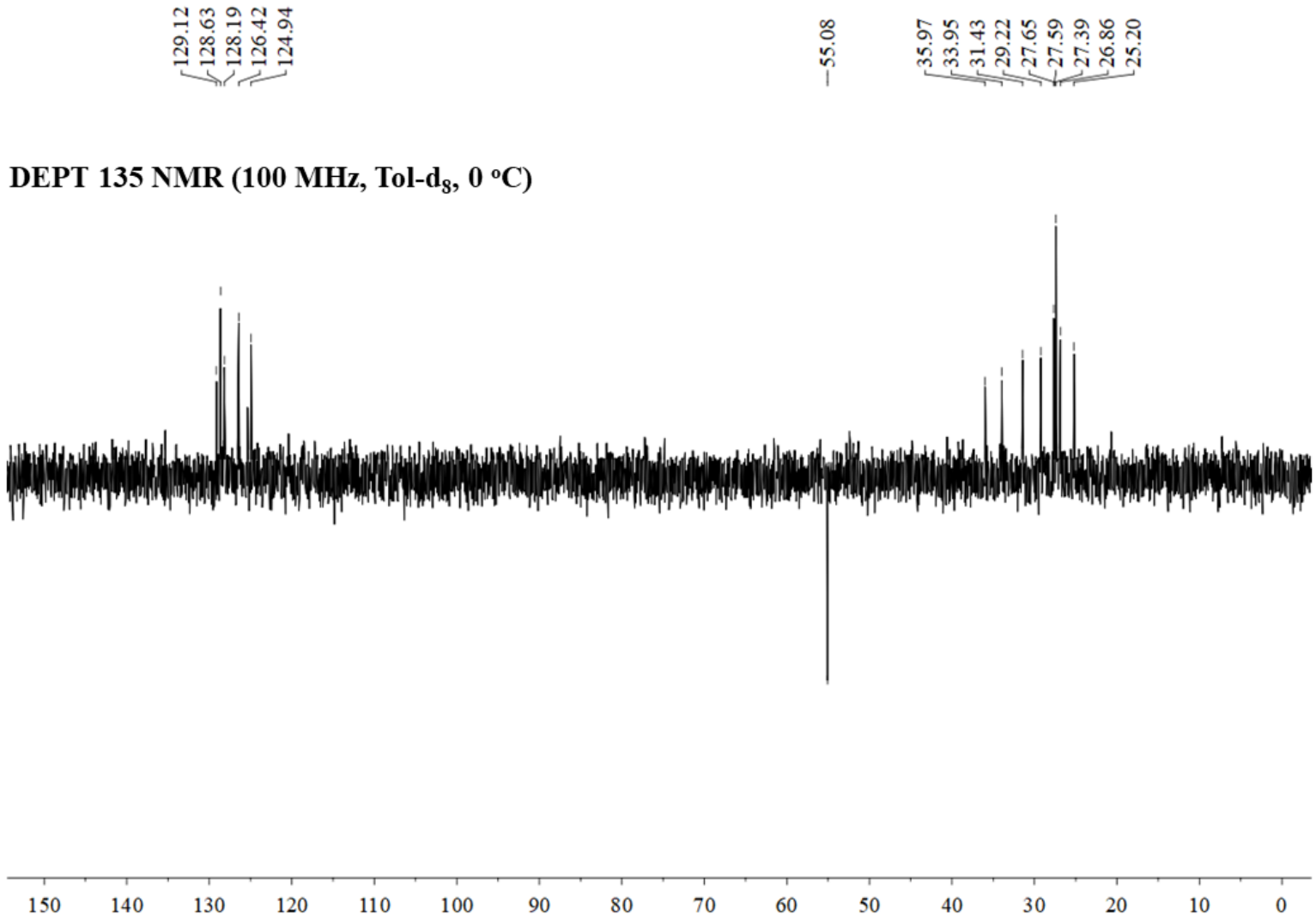


Fig. S4. DEPT135 NMR spectrum of **2a**.

VT NMR spectra and chemical shift vs. T fitting for 2a.

The ^{1}H NMR spectra were recorded in toluene-d_8. Peak positions were picked by fitting in MestReNova software. Curve fitting was performed using Origin software using the equation f(T) = A+1000000*B/(T*(3+exp(C/T))).[4,5]

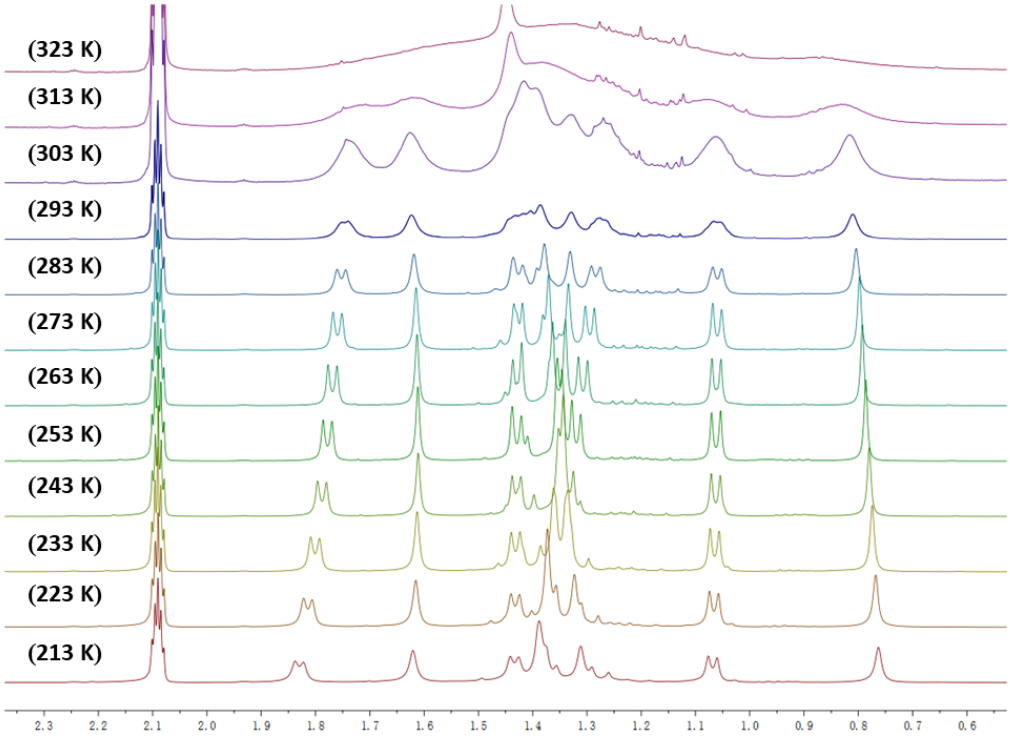
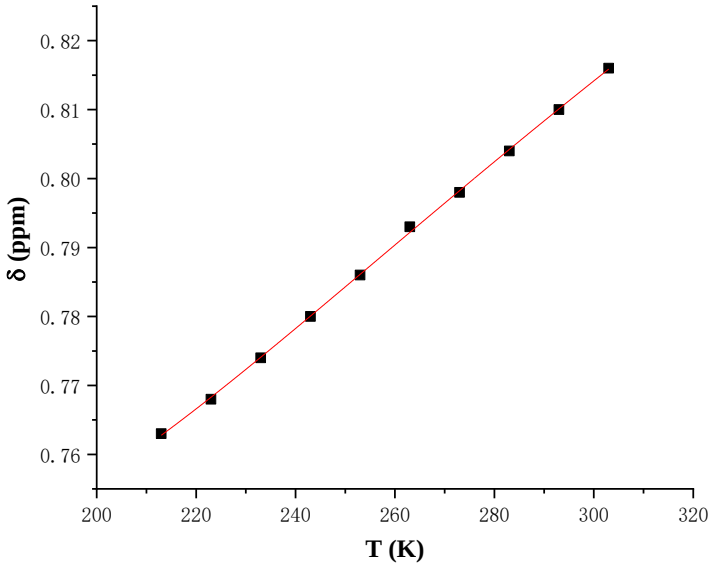


Fig. S5. Variable temperature ^{1}H NMR spectra of **2a**.

Table S1. VT NMR chemical shifts of **2a**.

T (K)	δ (ppm)
213	0.763
223	0.768
233	0.774
243	0.780
253	0.786
263	0.793
273	0.798
283	0.804
293	0.810
303	0.816
313	(obscured)
323	(obscured)



$\Delta E_{T-S} = C*R$	
A	1.09723±0.01128
B	-4.59116E-4±2.20959E-5
C	263.45393 ± 6.04871
ΔE_{T-S}	**0.52 kcal mol^{-1}**

Fig. S6. Fits of data presented in Table S1 with fit coefficients displayed at right.

Crystallographic details

Single crystals of complex **1a** and **2a** suitable for X-ray diffraction analysis were grown as described in the experimental section. The single crystals were wrapped in mineral oil and then were frozen at low temperature. Data collections were performed on a Bruker D8 venture microsource diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 100 K. The structures were solved with the shelxs-97[6] or Olex2[7] and refined with the XL refinement package using Least Squares minimization. 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. Crystal data, data collection and processing parameters for **1a** and **2a**were summarized. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1910420 (**1a**), CCDC 1910434 (**2a**). Copies of these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The thermal ellipsoid plots were drawn by Ortep-3 v1.08.[8]

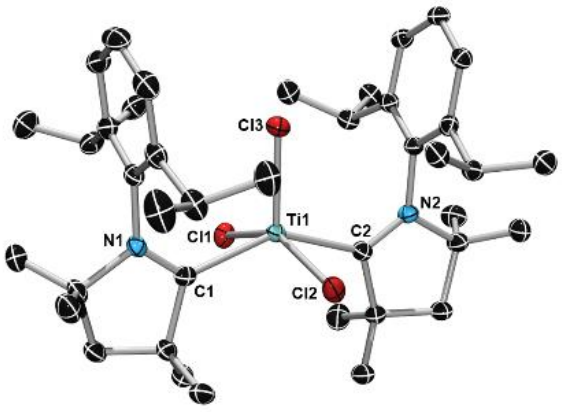


Figure S7. ORTEP drawing of **1a** with 50% thermal ellipsoids. H atoms are omitted for clarity.

Table S2. Crystal data and structure refinement for **1a**.

Identification code	**1a**
Empirical formula	$C_{40}H_{62}Cl_3N_2Ti$
Formula weight	725.16
Temperature/K	100.01
Crystal system	monoclinic
Space group	$P2_{1/c}$
a/Å	20.5112(8)
b/Å	11.5599(4)
c/Å	17.7631(6)
α/°	90
β/°	108.1970(10)
γ/°	90
Volume/Å^3	4001.1(2)
Z	4
ρ_{calc}mg/mm^3	1.204
μ/mm^{-1}	0.443
F(000)	1556.0
Crystal size/mm^3	0.15 × 0.1 × 0.05
Radiation	MoKα (λ = 0.71073)
2 Θ range for data collection	4.828 to 55.05°
Index ranges	$-26 \leq h \leq 26$, $-15 \leq k \leq 15$, $-23 \leq l \leq 23$
Reflections collected	48476
Independent reflections	9184 [R_{int} = 0.0720, R_{sigma} = 0.0516]
Data/restraints/parameters	9184/0/431
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0436, wR_2 = 0.0877
Final R indexes [all data]	R_1 = 0.0687, wR_2 = 0.0989
Largest diff. peak/hole / e Å^{-3}	0.41/-0.38

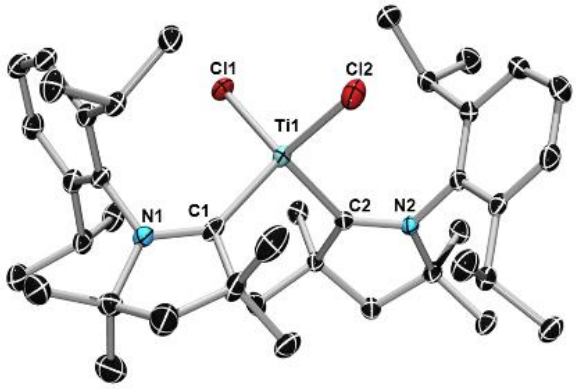


Figure S8. ORTEP drawing of **2a** with 50% thermal ellipsoids. H atoms are omitted for clarity.

Table S3. Crystal data and structure refinement for **2a**.

Identification code	**2a**
Empirical formula	$C_{40}H_{62}Cl_2N_2Ti$
Formula weight	689.71
Temperature/K	99.99
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.2202(18)
b/Å	17.655(2)
c/Å	17.168(3)
α/°	90
β/°	108.957(5)
γ/°	90
Volume/Å^3	3789.9(9)
Z	4
ρ_{calc}mg/mm^3	1.209
μ/mm^{-1}	0.396
F(000)	1488.0
Crystal size/mm^3	0.07 × 0.06 × 0.05
Radiation	MoKα (λ = 0.71073)
2 Θ range for data collection	4.614 to 52.044°
Index ranges	-16 ≤ h ≤16, -21 ≤ k ≤ 21, -21 ≤ l ≤ 21
Reflections collected	112043
Independent reflections	7473 [R_{int} = 0.1037, R_{sigma} = 0.0368]
Data/restraints/parameters	7473/0/422
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0461, wR_2 = 0.1102
Final R indexes [all data]	R_1 = 0.0635, wR_2 = 0.1249
Largest diff. peak/hole / e Å^{-3}	1.32/-0.68

Computational details

All calculations were performed using the Gaussian 09 software package.[9] All structures were optimized using the TPSSh functional[10, 11] which has a good credit in producing accurate singlet-triplet gaps.[12] The def2-TZVP basis set was used for Ti and Cl,[13] 6-311G* for the carbene carbons and their neighboring nitrogen atoms, and 6-31G* for the rest of atoms.[14, 15] Stability check has been performed to ensure all of the located electronic states are the correct states associated with the spin multiplicity, and frequency calculation has also been performed to verify all optimized structures are local minima without imaginary frequencies and to provide free energies at various temperatures. SNO analysis was performed using in-house code.[16]

Table S4. Calculated singlet-triplet free energy gap at various temperatures.

T(K)	G_T-G_S(kcal/mol)
0	0.30
10	0.27
20	0.24
30	0.20
40	0.15
50	0.10
60	0.05
70	-0.01
80	-0.07
90	-0.13
100	-0.19

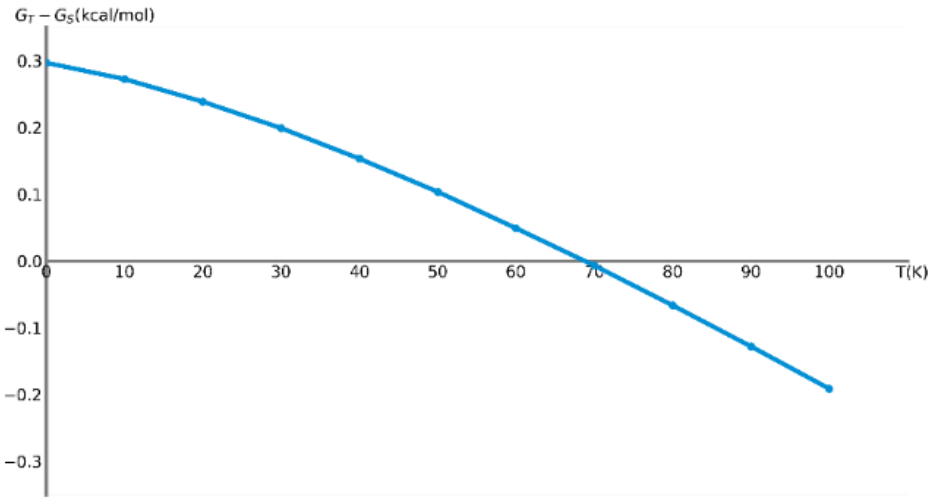


Figure S9. Calculated singlet-triplet free energy gap at various temperatures.

We have optimized the structure of **1a** and compared the calculation results with its simplified analog **1a'** in which the *i*Pr substituents are replaced with Me. The two geometries are close to each other, indicating that it is the electronic factor that determines the structure observed. The structure is better described as slightly distorted square pyramidal. The single d electron occupies a d_δ orbital viewing along the apical Cl ligand (Fig. S10).

Table S5. Selected structural parameters calculated for **1a** and its simplified analog **1a'** in which the ^{i}Pr substituents are replaced with Me, together with comparison against experimental values.

	$TiCl_3$(cAAC-iPr)$_2$ (**1a**)		$TiCl_3$(cAAC-Me)$_2$ (**1a'**)
	exp	calc	calc
Ti-C(cAAC)	2.30	2.30	2.27
Ti-Cl_{ax}	2.23	2.24	2.23
Ti-Cl_{eq}	2.35-2.36	2.37	2.38
Cl_{ax}-Ti-Cl_{eq}	104.3-106.2	104.9	102.9
Cl_{ax}-Ti-C(cAAC)	105.7-106.9	108.5	110.8
Cl_{eq}-Ti-Cl_{eq}	149.5	150.2	154.2
C(cAAC)-Ti- C(cAAC)	147.4	143.1	138.4

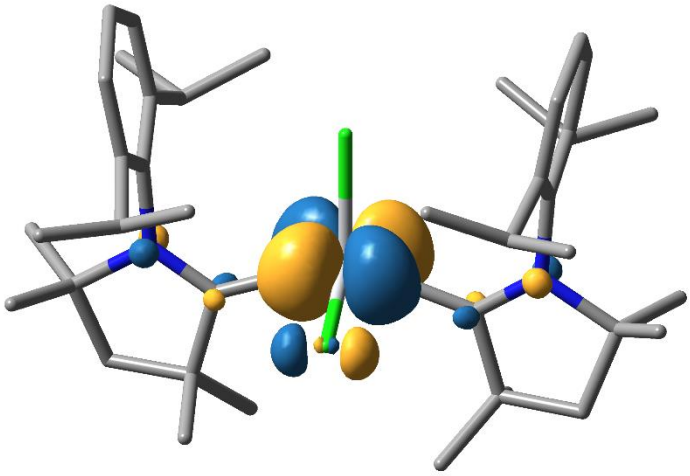


Figure S10. The spin natural orbital (SNO) calculated for **1a**, which accommodates the single d electron of the complex.

Cartesian coordinates of all calculated structures

Optimized Singlet Biradical State

Ti	0.00001400	0.00000900	0.57766600
Cl	-1.29586000	-1.41905300	1.78101900
Cl	1.29586200	1.41909500	1.78101600
C	1.27881900	-1.15726200	-0.64291900
N	1.52824500	-2.50203200	-0.69935800
C	2.59722700	-2.93165900	-1.69968400
C	2.12171100	-4.06169400	-2.61863800
H	2.91165300	-4.26917300	-3.35046700
H	1.21769100	-3.78699600	-3.16816500
H	1.93790300	-4.98148300	-2.05554800
C	3.87498300	-3.42421900	-1.00064600
H	4.32918600	-2.66272800	-0.36484700
H	4.60840900	-3.70974700	-1.76376900
H	3.66220200	-4.30864100	-0.39201600
C	2.79506800	-1.63123400	-2.48702200
H	3.83549700	-1.50515800	-2.80700200
H	2.17157200	-1.65735900	-3.38966200
C	2.32170400	-0.48069200	-1.57296500
C	1.75911700	0.66955100	-2.41963600
H	2.55949000	1.10658000	-3.03209800
H	1.34117400	1.45641900	-1.78808000
H	0.96918500	0.31936100	-3.09009000
C	3.50247200	0.07690500	-0.73901900
H	4.26255800	0.48603800	-1.41760500
H	3.97826600	-0.69253700	-0.12563300
H	3.17107100	0.87261300	-0.06828200
C	-1.27879000	1.15726400	-0.64294300
N	-1.52824500	2.50203100	-0.69935600
C	-2.59722200	2.93165900	-1.69968700
C	-3.87499500	3.42418300	-1.00065400
H	-4.60842000	3.70970600	-1.76378100
H	-3.66223800	4.30860200	-0.39201100
H	-4.32918800	2.66267500	-0.36486900
C	-2.12171400	4.06172300	-2.61861000
H	-1.21768500	3.78705000	-3.16813400
H	-1.93792600	4.98150200	-2.05549800
H	-2.91165200	4.26920600	-3.35044300
C	-2.79502900	1.63124900	-2.48705600
H	-2.17152700	1.65740800	-3.38969100
H	-3.83545300	1.50515800	-2.80704700
C	-2.32164700	0.48069600	-1.57302300
C	-3.50240800	-0.07694400	-0.73909700
H	-4.26248100	-0.48608100	-1.41769500

H	-3.97822200	0.69247600	-0.12569900
H	-3.17099400	-0.87265600	-0.06837200
C	-1.75902600	-0.66951300	-2.41971500
H	-1.34106300	-1.45638200	-1.78817400
H	-0.96910300	-0.31928700	-3.09016100
H	-2.55938500	-1.10655100	-3.03218900
C	1.04563700	-3.49835800	0.24996400
C	0.00398300	-4.39641000	-0.10759200
C	-0.31958900	-5.43424900	0.77905800
H	-1.11542300	-6.12396900	0.51052100
C	0.33339400	-5.58877100	1.99605300
H	0.06673400	-6.40327100	2.66429300
C	1.31122600	-4.67037300	2.36019000
H	1.79789400	-4.76454400	3.32724400
C	1.68538900	-3.61482600	1.51650300
C	-0.87616400	-4.25905800	-1.34920200
H	-0.48848200	-3.43444400	-1.95501500
C	-2.32079900	-3.90680000	-0.93110200
H	-2.77844100	-4.74254000	-0.38832300
H	-2.93423300	-3.70632400	-1.81809100
H	-2.34670400	-3.03283900	-0.27681200
C	-0.92198500	-5.53247100	-2.21953000
H	0.06843700	-5.86341100	-2.54266000
H	-1.52850600	-5.34766800	-3.11452300
H	-1.38934200	-6.36154100	-1.67541500
C	2.72468100	-2.63640300	2.06323500
H	2.93248000	-1.88509300	1.29674700
C	2.17696600	-1.89413900	3.30175000
H	1.22488900	-1.40110100	3.09429000
H	2.89397500	-1.13231700	3.62815600
H	2.01940600	-2.59218000	4.13324600
C	4.04986500	-3.32476000	2.45473500
H	3.90045200	-4.01007900	3.29751400
H	4.77867500	-2.56983200	2.77354700
H	4.48865700	-3.89865100	1.63386900
C	-1.04565600	3.49835500	0.24997900
C	-1.68542500	3.61481100	1.51651000
C	-1.31128500	4.67036100	2.36020500
H	-1.79796700	4.76452600	3.32725200
C	-0.33345800	5.58877100	1.99608200
H	-0.06681600	6.40327200	2.66432800
C	0.31954500	5.43425700	0.77909700
H	1.11537600	6.12398500	0.51057300
C	-0.00400400	4.39641700	-0.10756100
C	-2.72470700	2.63637000	2.06323100
H	-2.93248400	1.88505600	1.29674000

C	-4.04990700	3.32470200	2.45472100
H	-3.90051200	4.01002700	3.29749800
H	-4.77870300	2.56976100	2.77353000
H	-4.48870600	3.89858200	1.63384900
C	-2.17698900	1.89411800	3.30175200
H	-1.22489600	1.40110400	3.09430200
H	-2.89398200	1.13227700	3.62814700
H	-2.01945700	2.59216100	4.13325000
C	0.87616000	4.25908000	-1.34916100
H	0.48849600	3.43446000	-1.95497900
C	0.92197100	5.53249600	-2.21948600
H	-0.06845100	5.86342400	-2.54262300
H	1.52850400	5.34770200	-3.11447300
H	1.38931300	6.36156900	-1.67536400
C	2.32079600	3.90684400	-0.93104700
H	2.77841700	4.74258900	-0.38825900
H	2.93424200	3.70638400	-1.81803100
H	2.34671100	3.03288000	-0.27676100

Optimized Triplet State

Ti	-0.00001500	0.00010800	0.44810300
Cl	0.68000400	-1.81532000	1.74781000
Cl	-0.68021700	1.81563200	1.74757100
C	1.69917900	0.89925600	-0.72981600
N	3.01717900	0.67692400	-0.67122300
C	3.89089900	1.55219500	-1.58199500
C	4.88416400	0.72807300	-2.40539200
H	5.44717000	1.41330200	-3.05010200
H	4.37572000	0.00520400	-3.04800700
H	5.60030200	0.20266500	-1.76621100
C	4.69465800	2.57007100	-0.76059700
H	4.05833000	3.21292500	-0.14941800
H	5.26382700	3.20655700	-1.44784200
H	5.40766400	2.05767000	-0.10794000
C	2.81925100	2.19256100	-2.47488000
H	3.06674500	3.23083900	-2.72079200
H	2.75317000	1.63639400	-3.41852500
C	1.48547500	2.07225100	-1.70490000
C	0.31427700	1.83266800	-2.67033300
H	0.17302900	2.71098900	-3.31373700
H	-0.61941000	1.65489600	-2.12686800
H	0.50589200	0.96769800	-3.31303600
C	1.20172000	3.35823100	-0.88908300
H	1.06780600	4.19913800	-1.58181200
H	2.02559500	3.60299800	-0.21233900

H	0.30263800	3.25346600	-0.27897300
C	-1.69912800	-0.89926400	-0.72983500
N	-3.01713700	-0.67703000	-0.67117200
C	-3.89085000	-1.55240900	-1.58185300
C	-4.69449400	-2.57029900	-0.76036300
H	-5.26362000	-3.20688700	-1.44754900
H	-5.40753400	-2.05791400	-0.10773000
H	-4.05809600	-3.21304900	-0.14914800
C	-4.88421700	-0.72839200	-2.40523200
H	-4.37585500	-0.00553500	-3.04792400
H	-5.60034300	-0.20298500	-1.76603900
H	-5.44722400	-1.41369300	-3.04986500
C	-2.81920800	-2.19273800	-2.47477300
H	-2.75322900	-1.63661400	-3.41845000
H	-3.06663600	-3.23104800	-2.72061700
C	-1.48539900	-2.07228300	-1.70487900
C	-1.20152000	-3.35818900	-0.88898500
H	-1.06754100	-4.19912700	-1.58166200
H	-2.02536500	-3.60298200	-0.21221500
H	-0.30244400	-3.25330400	-0.27888900
C	-0.31426700	-1.83268600	-2.67038500
H	0.61943500	-1.65482100	-2.12697600
H	-0.50596900	-0.96776700	-3.31313300
H	-0.17300200	-2.71103700	-3.31374400
C	3.69378500	-0.21043700	0.27260600
C	4.11910600	-1.49545900	-0.15219700
C	4.91536000	-2.25172700	0.71882200
H	5.24405500	-3.23943200	0.40703400
C	5.27437000	-1.77734300	1.97577000
H	5.89860400	-2.37843300	2.63143200
C	4.79383400	-0.54421500	2.40038400
H	5.03031600	-0.19580900	3.40190300
C	3.99055100	0.26092000	1.57880900
C	3.67460200	-2.16610500	-1.45111200
H	3.10300100	-1.43966700	-2.03918800
C	2.73840300	-3.34899800	-1.12233000
H	3.29158500	-4.14392300	-0.60799700
H	2.32054200	-3.77212700	-2.04419000
H	1.92347000	-3.03760900	-0.46502800
C	4.84524700	-2.68703000	-2.31005800
H	5.57239500	-1.90806200	-2.55526100
H	4.46039600	-3.10406600	-3.24863800
H	5.38093600	-3.49144300	-1.79285400
C	3.43091100	1.54197700	2.19788400
H	2.82326100	2.06125200	1.45005400
C	2.50415900	1.19390300	3.38425200

H	1.73110400	0.47728600	3.09997000
H	2.01200300	2.10142800	3.74995100
H	3.08305500	0.76022800	4.20935900
C	4.52811000	2.50342500	2.70139000
H	5.10337900	2.04672100	3.51548600
H	4.06420600	3.41335600	3.10005300
H	5.23415100	2.79549100	1.91888400
C	-3.69376500	0.21039600	0.27258400
C	-3.99053500	-0.26085500	1.57882400
C	-4.79385700	0.54432700	2.40031500
H	-5.03034600	0.19600000	3.40186000
C	-5.27441500	1.77740800	1.97559100
H	-5.89867600	2.37853800	2.63119100
C	-4.91539200	2.25169600	0.71861100
H	-5.24410400	3.23936700	0.40673500
C	-4.11911000	1.49537300	-0.15233500
C	-3.43084400	-1.54182400	2.19803800
H	-2.82313000	-2.06113300	1.45028200
C	-4.52800000	-2.50329100	2.70160100
H	-5.10333600	-2.04653400	3.51562000
H	-4.06405000	-3.41314500	3.10038700
H	-5.23398700	-2.79549700	1.91910000
C	-2.50416400	-1.19357600	3.38441300
H	-1.73115500	-0.47692400	3.10010100
H	-2.01195000	-2.10103200	3.75020500
H	-3.08312900	-0.75988100	4.20946100
C	-3.67463300	2.16591700	-1.45131300
H	-3.10300500	1.43944700	-2.03932500
C	-4.84530700	2.68671400	-2.31030000
H	-5.57244000	1.90770200	-2.55540500
H	-4.46048200	3.10365800	-3.24893100
H	-5.38100800	3.49117000	-1.79317400
C	-2.73848600	3.34888600	-1.12265500
H	-3.29170000	4.14382900	-0.60838200
H	-2.32067000	3.77195400	-2.04456300
H	-1.92352200	3.03760300	-0.46534100

1a ($TiCl_3(cAAC\text{-}^iPr)_2$)

Ti	0.00000100	0.55464900	0.00001000
Cl	0.11185200	1.16247000	-2.28520800
Cl	-0.11184400	1.16235700	2.28525900
Cl	-0.00000400	-1.68235900	-0.00003600
N	3.30156800	0.57514000	-0.07029700
C	2.18437500	1.28385700	-0.00455600

C	2.58715000	2.77402900	0.02114500
C	1.78081100	3.67654700	-0.92735500
H	1.86206900	3.34384800	-1.96487100
H	2.16910900	4.70071400	-0.84987800
H	0.71918100	3.70182100	-0.67158800
C	2.42755700	3.31163800	1.46591100
H	1.38090600	3.32132800	1.77463500
H	2.82068000	4.33555300	1.50181500
H	2.97364900	2.70740900	2.19672500
C	4.07154500	2.78517200	-0.41056400
H	4.13765100	3.00424200	-1.48297900
H	4.64829000	3.55006500	0.11998600
C	4.61583900	1.38082900	-0.14335400
C	5.39812200	1.27135200	1.17063200
H	4.81602800	1.59498100	2.03622200
H	6.28747500	1.90790700	1.09990900
H	5.73403800	0.24362100	1.33189600
C	5.52603600	0.90729500	-1.27758900
H	5.84662600	-0.12928400	-1.13648700
H	6.42124300	1.54036200	-1.28133100
H	5.04057200	1.00692200	-2.25056100
C	3.41739100	-0.88442400	-0.00400200
C	3.51142800	-1.62990800	-1.20870200
C	3.77951900	-3.00296000	-1.11068700
H	3.84940400	-3.58814800	-2.02335500
C	3.94361300	-3.63220300	0.11812500
H	4.15924300	-4.69631400	0.16543700
C	3.79777800	-2.89306300	1.28606300
H	3.88181300	-3.39236900	2.24732700
C	3.52328400	-1.51731400	1.26280100
C	3.27155500	-0.84285100	2.61275700
H	3.05988700	0.21787300	2.44671000
C	2.02523700	-1.45876200	3.28395400
H	1.15848900	-1.41793600	2.62420500
H	1.78504900	-0.90680400	4.19946300
H	2.20912700	-2.50620500	3.55390100
C	4.45765100	-0.97306200	3.59220300
H	4.63355300	-2.02336900	3.85326200
H	4.22469000	-0.44069300	4.52204000
H	5.39303800	-0.56922800	3.19572300
C	3.26536100	-1.07214700	-2.61156500
H	3.09208400	0.00621400	-2.53970000
C	1.99271000	-1.69899000	-3.21916100
H	2.12733900	-2.77719800	-3.37145000
H	1.78146500	-1.24031500	-4.19188400
H	1.12849700	-1.54560400	-2.57302000

C	4.44018400	-1.33632200	-3.57883200
H	5.40145600	-0.98044100	-3.19811100
H	4.24588000	-0.84080500	-4.53751400
H	4.54187900	-2.40887700	-3.78260100
N	-3.30156600	0.57514000	0.07032500
C	-2.18437100	1.28385500	0.00460300
C	-2.58714100	2.77403000	-0.02103500
C	-1.78078800	3.67650500	0.92749400
H	-1.86203800	3.34376600	1.96499700
H	-2.16907900	4.70067800	0.85006100
H	-0.71916000	3.70178200	0.67171600
C	-2.42755900	3.31169800	-1.46577900
H	-1.38091000	3.32140200	-1.77451100
H	-2.82068400	4.33561400	-1.50163900
H	-2.97365600	2.70749900	-2.19661500
C	-4.07153100	2.78516100	0.41069000
H	-4.13762400	3.00418600	1.48311500
H	-4.64827800	3.55007800	-0.11982100
C	-4.61583300	1.38083100	0.14342700
C	-5.52602300	0.90725500	1.27764900
H	-5.84661800	-0.12931800	1.13650800
H	-6.42122900	1.54032400	1.28142200
H	-5.04055300	1.00684100	2.25062200
C	-3.41739500	-0.88442100	0.00396500
C	-3.52329200	-1.51725300	-1.26286700
C	-3.27156700	-0.84272700	-2.61279200
H	-3.05990100	0.21799000	-2.44669700
C	-4.45766700	-0.97289400	-3.59223900
H	-4.63357000	-2.02318900	-3.85334700
H	-4.22471100	-0.44048200	-4.52205300
H	-5.39305300	-0.56907900	-3.19573700
C	-2.02525100	-1.45860400	-3.28402100
H	-1.15850100	-1.41780500	-2.62427400
H	-1.78506800	-0.90660500	-4.19950700
H	-2.20913800	-2.50603700	-3.55401400
C	-3.79778700	-2.89300000	-1.28619200
H	-3.88182400	-3.39226200	-2.24747900
C	-3.94362100	-3.63219400	-0.11828800
H	-4.15925300	-4.69630300	-0.16564800
C	-3.77952400	-3.00300700	1.11055400
H	-3.84941000	-3.58823600	2.02319400
C	-3.51143100	-1.62996000	1.20863000
C	-3.26535900	-1.07226400	2.61151900
H	-3.09207800	0.00609900	2.53970400
C	-4.44018300	-1.33647900	3.57877500
H	-5.40145300	-0.98057700	3.19807100

H	-4.24587600	-0.84100700	4.53748000
H	-4.54188200	-2.40904300	3.78249500
C	-1.99271100	-1.69914100	3.21908500
H	-2.12734500	-2.77735600	3.37132600
H	-1.78146300	-1.24051200	4.19182900
H	-1.12849900	-1.54573000	2.57295000
C	-5.39812800	1.27141100	-1.17055700
H	-4.81604200	1.59507300	-2.03614000
H	-6.28747900	1.90796500	-1.09979900
H	-5.73404900	0.24368700	-1.33186000

1a' ($TiCl_3(cAAC\text{-}Me)_2$)

Ti	0.00000300	-0.24727600	-0.00000300
Cl	0.05867000	-0.77895600	2.31883200
Cl	-0.05863100	-0.77894500	-2.31884000
Cl	-0.00002700	1.98660400	0.00000200
N	3.22122600	-0.31938800	0.07459000
C	2.12502300	-1.05550800	0.02909800
C	2.56307700	-2.52994700	0.03595300
C	1.77218400	-3.41077900	1.01707800
H	1.83257500	-3.02798000	2.03908200
H	2.18300500	-4.42852300	0.99204200
H	0.71430600	-3.46993600	0.74847800
C	2.39784800	-3.10117600	-1.39441400
H	1.35308000	-3.08767700	-1.71130100
H	2.76203100	-4.13630300	-1.40445600
H	2.96636600	-2.52937000	-2.13430500
C	4.05671700	-2.49128600	0.45052300
H	4.14388200	-2.70434800	1.52253000
H	4.64994700	-3.24000500	-0.08504700
C	4.55558000	-1.06715900	0.17009200
C	5.33915400	-0.94224700	-1.14564300
H	4.77877300	-1.33190200	-1.99854400
H	6.26895900	-1.51534900	-1.05545500
H	5.60471500	0.10086300	-1.34463900
C	5.42497500	-0.52719800	1.31187100
H	5.69782300	0.52111200	1.15328400
H	6.34903400	-1.11586600	1.34838300
H	4.92384600	-0.62340600	2.27793100
C	3.25780100	1.13233800	-0.01927300
C	3.26592600	1.89598900	1.16692100
C	3.40398200	3.28570500	1.05184600
H	3.40351800	3.88588600	1.95867900
C	3.50907700	3.90246000	-0.19193300
H	3.61056000	4.98230500	-0.25948500
C	3.44078100	3.13228200	-1.35022500

H	3.47048300	3.61280500	-2.32523600
C	3.30678200	1.73842600	-1.29363300
C	3.16993700	0.97989700	-2.59557300
H	2.71248200	-0.00163500	-2.46251000
H	2.52280000	1.54270600	-3.27537200
H	4.13984000	0.85385600	-3.09315100
C	3.06690100	1.30905000	2.54654800
H	2.75109800	0.26559700	2.51915900
H	2.27865800	1.86466200	3.06497100
H	3.98071100	1.39083300	3.14877800
N	-3.22121900	-0.31940900	-0.07459000
C	-2.12500400	-1.05551200	-0.02909700
C	-2.56303600	-2.52995900	-0.03595100
C	-1.77212500	-3.41078300	-1.01706900
H	-1.83251600	-3.02798700	-2.03907400
H	-2.18293300	-4.42853200	-0.99203300
H	-0.71424900	-3.46992500	-0.74846200
C	-2.39780800	-3.10118300	1.39441800
H	-1.35304100	-3.08767400	1.71130800
H	-2.76198200	-4.13631300	1.40446100
H	-2.96633200	-2.52938000	2.13430700
C	-4.05667400	-2.49131900	-0.45053100
H	-4.14382600	-2.70437600	-1.52254000
H	-4.64989600	-3.24005000	0.08503000
C	-4.55556000	-1.06720200	-0.17009800
C	-5.42496000	-0.52725300	-1.31187900
H	-5.69783400	0.52105000	-1.15328900
H	-6.34900500	-1.11594200	-1.34840100
H	-4.92382200	-0.62344400	-2.27793700
C	-3.25782200	1.13231600	0.01927600
C	-3.30681900	1.73839900	1.29363700
C	-3.16995600	0.97986900	2.59557400
H	-2.71245700	-0.00164300	2.46251100
H	-4.13985800	0.85378400	3.09314200
H	-2.52285100	1.54270400	3.27538400
C	-3.44085100	3.13225200	1.35023100
H	-3.47056600	3.61277200	2.32524300
C	-3.50916400	3.90243100	0.19194100
H	-3.61067400	4.98227300	0.25949500
C	-3.40405000	3.28568100	-1.05183900
H	-3.40359700	3.88586400	-1.95867100
C	-3.26595900	1.89596900	-1.16691700
C	-3.06690400	1.30903600	-2.54654200
H	-2.75108800	0.26558700	-2.51915100
H	-3.98070500	1.39080900	-3.14878700
H	-2.27865900	1.86465900	-3.06494900

C	-5.33914100	-0.94230500	1.14563400
H	-4.77875600	-1.33195200	1.99853700
H	-6.26893600	-1.51542200	1.05544300
H	-5.60472000	0.10080000	1.34463100

References

1. Jones, N. A.; Liddle, S. T.; Wilson, C.; Arnold, P. L. Organometallics 2007, 26, 755-757.
2. Jazzar, R.; Dewhurst, R. D.; Bourg, J. B.; Donnadieu, B.; Canac, Y.; Bertrand, G. Angew. Chem., Int. Ed. 2007, 46, 2899-2902.
3. Chakraborty, S.; Chattopadhyay, J.; Guo, W.; Billups, W. E. Angew. Chem., Int. Ed. 2007, 46, 4486-4488.
4. Lemon, C. M.; Huynh, M.; Maher, A. G.; Anderson, B. L.; Bloch, E. D.; Powers, D. C.; Nocera, D. G. Angew. Chem. Int. Ed. 2016, 55, 2176-2180.
5. Guennic, B. Le; Floyd, T.; Galan, B. R.; Autschbach, J.; Keister, J. B. Inorg. Chem. 2009, 48, 5504-5511.
6. Sheldrick, G. M. SHELXTL 5.10 for Windows NT: *Structure Determination Software Programs*; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997.
7. (a) Sheldrick, G. M. *Acta Crystallogr*., 2008, A64, 112-122. (b) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K. and Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst*., 2009, 42, 339-341.
8. Farrugia, L. J. *J. Appl. Crystallogr*., 1997, 30, 565-565.
9. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö .; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision D.01; Gaussian, Inc.: Wallingford, CT, 2009.
10. Staroverov, V. N.; Scuseria, G. E.; Tao, J. M.; Perdew, J. P. J. Chem. Phys. 2003, 119, 12129-12137.
11. Tao, J. M.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. Phys. Rev. Lett. 2003, 91, 146401.
12. Cirera, J.; Via-Nadal, M.; Ruiz, E. Inorganic chemistry. 2018, 57, 14097-14105.
13. Weigend, F.; Ahlrichs, R. Phys. Chem. Chem. Phys. 2005, 7, 3297-3305.

14. Hehre, W. J.; Ditchfield, R.; Pople, J. A. J. Chem. Phys. 1972, 56, 2257-2261.
15. Hariharan, P. C.; Pople, J. A. Theor. Chim. Acta. 1973, 28, 213-222.
16. Sheong, F. K.; Zhang, J.-X.; Lin, Z. J. Comput. Chem. 2019, 40, 1172-1184.