Design Platform for Sustainable Catalysis with Radicals: Electrochemical Activation of Cp₂TiCl₂ for Catalysis Unveiled

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1. General Information

All reactions involving air- or moisture sensitive compounds were prepared in oven dried glassware under inert atmosphere (Ar) using standard Schlenk and vacuum line technique. All chemicals were purchased from abcr GmbH, TCI GmbH, Alfa Aesar, Fluka, Acros, Flourochem or Sigma Aldrich and were used without further purification. Solvents used in manipulations under inert atmosphere were either dried and deoxygenated by distillation (THF over Na/K-alloy) before use or purified inside a M-Braun MB-SPS-800 solvent purification system and used after degasification. The NMR analysis was carried out on a Bruker DPX 300 MHz, Bruker 400 MHz or Bruker 500 MHz spectrometer. $^1$H and $^{13}$C NMR chemical shifts were specified in ppm and calibrated by using the residual undeuterated solvent as internal reference [$^1$H NMR: CHCl$_3$ (7.26 ppm), C$_6$HD$_5$ (7.16 ppm), DMSO-d$_5$ (2.50 ppm), CH$_2$CN (1.94 ppm), THF-d$_7$ (1.72 ppm, 3.58 ppm); $^{13}$C NMR: CDCl$_3$ (77.0 ppm), C$_6$D$_6$ (128.0 ppm), DMSO-d$_6$ (39.5 ppm), CD$_2$CN (118.3 ppm), THF-d$_8$ (25.3 ppm, 67.2 ppm)]. High resolution mass spectra analysis was measured on a Thermoquest MAT 95 CL or Thermo Fisher Scientific LTQ Orbitrap XL instrument. IR spectra were obtained on an ATR-IR Spectrometer Thermo Electron Nicolet™ 380 instrument as neat film. CHNS analysis was measured on an Elementar Analysesysteme varioMICRO instrument. Silica gel (230-400 mesh) supplied by Merck and Macherey-Nagel or neutral aluminum oxide 90 supplied by Merck was used as stationary phase for column chromatography.

2. Synthesis of Substrates

The substrate 1 was prepared according to the literature procedure. The additives $L_1$ and $L_2$ were synthesized following the cited literature. Analytical data of the corresponding products can also be found in these references. $L_3$ was synthesized in analogy to the cited literature.

2.1 Synthesis of $N,N'-(1,2$-phenylene)$\text{bis}(3,5$-bis(trifluoromethyl)-benzenesulfonamide) $L_3$

ortho-Phenylenediamine (0.98 g, 9.0 mmol, 1.0 eq) was dissolved in dry pyridine (15 mL) and the mixture was cooled to 0 °C. Then, 3,5-bis(trifluoromethyl)benzenesulfonyl chloride (5.63 g, 18.0 mmol, 2.0 eq.) was added. After 30 min the cooling bath was removed and the reaction stirred at room temperature for 19 h. Water (200 mL) was added and the mixture was heated to 45 °C for 1 h. The solvent was removed under reduced pressure at 50 °C. The crude product was recrystallised from EtOH/H$_2$O 4:1 and dried in vacuo at 100 °C. The product was obtained as a slightly red solid (4.85 g, 7.35 mmol, 82%).

$^1$H NMR (500 MHz, THF-d8, 298 K): $\delta$ [ppm] = 8.94 (s, 2H), 8.32 (s, 2H), 8.18 (s, 4H), 7.10 (m, 2H), 6.99 (m, 2H).
$^{13}$C NMR (125 MHz, THF-d8, 298 K): $\delta$ [ppm] = 143.3 (2C), 133.4 (q, $^2J_{C,F} = 34.2$ Hz, 4C), 132.3 (2C), 129.0 (4C), 128.5 (2C), 127.8 (2C), 126.7 (2C), 123.9 (q, $^3J_{C,F} = 237.0$ Hz, 4C).

$^{19}$F NMR (470 MHz, THF-d8, 298 K): $\delta$ [ppm] = −63.83 (12F).

IR (pure, ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3230 (m), 3106 (w), 1736 (w), 1348 (s), 1320 (s), 1278 (s), 1104 (s), 904 (s), 723 (s).

Mp.: 210 – 212 °C.

HR MS (ESI) [M-H]: m/z calc. for C$_{22}$H$_{11}$F$_{12}$N$_2$O$_4$S$_2$: 658.9974, found: 658.9974.

CHNS calc. for C$_{22}$H$_{11}$F$_{12}$N$_2$O$_4$S$_2$: C: 40.01, H: 1.83, N: 4.24, S: 9.71; found: C: 40.14, H: 2.03, N: 4.24, S: 9.89.

The data are in agreement with the literature.$^{[S4]}$
3. Cyclic Voltammetry Experiments

3.1 General Information

The chemicals tetrabutylammonium hexafluorophosphate (N\textsubscript{Bu}\textsubscript{4}PF\textsubscript{6}), tetrabutylammonium chloride (N\textsubscript{Bu}\textsubscript{4}Cl) and AgNO\textsubscript{3} were purchased in electrochemical grade from Aldrich and stored in a glovebox under an inert atmosphere (Ar).

All cyclic voltammetry experiments were carried out in a glovebox and were performed by a 1400D Electrochemical Analyzer (CH-Instruments). A glassy carbon disk of 1 mm diameter was used as working electrode material. The surface of the working electrode was polished with diamond paste (0.25 µm) provided by Struers followed by cleaning in an ethanol bath. A platinum coil melted into glass served as the counter electrode and the reference electrode consists of a silver wire immersed in a Pyrex tube containing N\textsubscript{Bu}\textsubscript{4}PF\textsubscript{6} (0.2 M) and N\textsubscript{Bu}\textsubscript{4}I (0.02 M) in THF separated from the main solution by a ceramic frit. The potentials were referenced against the Fc\textsuperscript{+}/Fc redox couple (the addition of 0.52 V to the potential will lead to the values of a SCE in 0.2 M N\textsubscript{Bu}\textsubscript{4}PF\textsubscript{6}/THF). The iR compensation mode of the CH-Instrument Electrochemical Analyzer was used for all cyclic voltammetry experiments.

3.2 General Procedure for Cyclic Voltammetry Experiments

The conducting salt N\textsubscript{Bu}\textsubscript{4}PF\textsubscript{6} (0.775 g, 0.200 mmol) was dissolved in the freshly distilled solvent (10 mL) and a magnetic stir bar was added to an oven dried cyclic voltammetry cell. Background measurements were conducted to reduce coulomb currents in the analysis by subtraction from the CVs recorded with analyte. Titanocene dichloride (5 mg, 0.02 mmol) was added to the cyclic voltammetry cell and CVs were recorded. After this, the indicated amount of additive was added. The cyclic voltammetry experiment was carried out at different sweep rates (0.05 Vs\textsuperscript{-1}, 0.1 Vs\textsuperscript{-1}, 0.2 Vs\textsuperscript{-1}, 0.5 Vs\textsuperscript{-1}, 1 Vs\textsuperscript{-1}, 2 Vs\textsuperscript{-1}, 5 Vs\textsuperscript{-1}, 10 Vs\textsuperscript{-1}, 20 Vs\textsuperscript{-1}, 50 Vs\textsuperscript{-1}) and the solution was stirred before measuring the respective sweep rate. At the end of the experiment a small amount of ferrocene (0.02 mmol) was added as an internal reference and the potential of the Fc\textsuperscript{+}/Fc redox couple was recorded.
3.3 CVs of the Additives L1 – L3

Here, the CVs of L1 – L3 at 0.2 and 2 V s⁻¹ are depicted for reference:
I / µA

E / V vs. Fc+/Fc [ν = 0.2 V s⁻¹]

[Cp₂Ti(III)Cl] - [Cp₂Ti(III)Cl] - L₃
[Cp₂Ti(III)Cl] - L₃
[Cp₂Ti(III)Cl] - [Cp₂Ti(III)Cl]

2 mM Cp₂TiCl₂
2 mM Cp₂TiCl₂ / 1 mM L₃
2 mM Cp₂TiCl₂ / 2 mM L₃
2 mM Cp₂TiCl₂ / 10 mM L₃

I / µA

E / V vs. Fc+/Fc [ν = 2 V s⁻¹]
4. Bulk Electrolysis

The divided bulk electrolysis cell was purchased from ALS which is distributed by C3 Prozess- und Analysentechnik GmbH in Germany. All controlled potential electrolysis experiments were carried out in a glovebox and were performed by a 1400D Electrochemical Analyzer (CH-Instruments). A glassy carbon mesh electrode was used as the cathode and a platinum wire immersed into a solution of CH$_3$CN/NBu$_4$PF$_6$ (0.2 M) and Cp$_2$TiCl$_2$ (0.01 M) served as anode. The reference electrode is composed of a silver wire and a solution of N Bu$_4$PF$_6$ (0.1 M) and AgNO$_3$ (0.01 M) in CH$_3$CN.

![Image of electrolysis cell](image1)

**Figure S1**: Bulk Electrolysis Cell used for catalyst activation.

### 4.1 Controlled-Potential Electrolysis in THF:

The bulk electrolysis cell (100 mL) was equipped with a stirring bar and N Bu$_4$PF$_6$ (4.65 g, 12.0 mmol), Cp$_2$TiCl$_2$ (149 mg, 0.60 mmol), additive (L1: 300 mg, 0.60 mmol, CPE1; L2: 342 mg, 0.60 mmol, CPE2; L3: 396 mg, 0.60 mmol, CPE3) and THF (60 mL) were added inside a glovebox. The electrodes were put inside the cell and connected to the potentiostat. The electrolysis was conducted at a controlled potential ($E = -1.4$ V), during the experiment the stirring was set to 260 rpm and the current flow was monitored. As an indicator the color change from red (Ti$^{IV}$) to green (Ti$^{III}$) was used and the electrochemical reduction was stopped when the current flow was below 1 mA. The electrolyzed solution was used as is for the arylation.

![Image of electrolysis process](image2)

**Figure S2**: Exemplary Electrolysis of Cp$_2$TiCl$_2$ and L2 in THF.
5. Catalytic Radical Arylation

5.1 General Procedure for the Arylation of Epoxides (GP 1):
A pressure stable Schlenk flask was filled with a stirring bar and the epoxide (1.0 eq.). The solution (CPE 1 to CPE3) containing the electrochemically generated \([\text{Cp}_2\text{Ti(III)}\text{Cl}]-\text{catalyst}\) (0.01 M, 0.1 eq.) was added inside a glovebox. After that, the reaction mixture was stirred for the indicated time at the indicated temperature. The reaction mixture was allowed to cool down to ambient temperature, the solvent was evaporated under reduced pressure and the crude product was purified by column chromatography.

5.2 Synthesis of (3-methyl-1-phenyl-2,3-dihydro-1-H-indol-3-yl)methanol 2

Following GP 1 epoxide 1 (120 mg, 0.5 mmol, 1.0 eq.) and the \(\text{Cp}_2\text{TiCl/THF}^\prime\)-catalyst system (CPE 1, 5 mL, 0.1 eq.) were stirred for 2 h at 90 °C (oil bath temperature). The crude product was purified by column chromatography (SiO\(_2\), CH:EA 9:1, \(R_f = 0.24\)) and the product 2 (71 mg, 0.30 mmol, 59%) was obtained as a colorless oil.

Following GP 1 epoxide 1 (120 mg, 0.5 mmol, 1.0 eq.) and the \(\text{Cp}_2\text{TiCl/THF}^\prime\)-catalyst system (CPE 2, 5 mL, 0.1 eq.) were stirred for 2 h at 75 °C (oil bath temperature). The crude product was purified by column chromatography (Al\(_2\)O\(_3\), CH:EA 8:2) and the product 2 (104 mg, 0.43 mmol, 87%) was obtained as a colorless oil.

Following GP 1 epoxide 1 (120 mg, 0.5 mmol, 1.0 eq.) and the \(\text{Cp}_2\text{TiCl/THF}^\prime\)-catalyst system (CPE 3, 5 mL, 0.1 eq.) were stirred for 2 h at 75 °C (oil bath temperature). The crude product was purified by column chromatography (Al\(_2\)O\(_3\), CH:EA 8:2) and the product 2 (106 mg, 0.44 mmol, 88%) was obtained as a colorless oil.

Following GP 1 epoxide 1 (120 mg, 0.5 mmol, 1.0 eq.) and the \(\text{Cp}_2\text{TiCl/THF}^\prime\)-catalyst system (CPE 3, 5 mL, 0.1 eq.) were stirred for 4 h at 75 °C (oil bath temperature). The crude product was purified by column chromatography (Al\(_2\)O\(_3\), CH:EA 8:2) and the product 2 (111 mg, 0.46 mmol, 93%) was obtained as a colorless oil.
Following GP 1 epoxide 1 (120 mg, 0.5 mmol, 1.0 eq.) and the \( \text{Cp}_2\text{TiCl/THF} \)-catalyst system (CPE 3, 5 mL, 0.1 eq.) were stirred for 5 h at 75 °C (oil bath temperature). The crude product was purified by column chromatography (Al\(_2\)O\(_3\), CH:EA 8:2) and the product 2 (110 mg, 0.46 mmol, 92%) was obtained as a colorless oil.

\(^1\)H NMR (500 MHz, C\(_6\)D\(_6\), 298 K): \( \delta \) [ppm] = 7.23 – 7.16 (m, 2H), 7.16 – 7.09 (m, 2H), 7.02 (ddd, \( J = 8.0, 7.4, 1.4 \) Hz, 1H), 6.93 (ddd, \( J = 7.3, 1.4, 0.6 \) Hz, 1H), 6.89 (tt, \( J = 7.3, 1.2 \) Hz, 1H), 6.75 (td, \( J = 7.4, 1.0 \) Hz, 1H), 3.62 (d, \( J = 9.3 \) Hz, 1H), 3.31 – 3.27 (m, 2H), 3.21 (d, \( J = 10.5 \) Hz, 1H), 1.14 (s, 3H), 0.94 (s, 1H).

\(^{13}\)C NMR (126 MHz, C\(_6\)D\(_6\), 298 K): \( \delta \) [ppm] = 147.1, 144.5, 136.3, 129.5, 123.6, 121.2, 119.4, 118.0, 108.9, 68.9, 61.8, 45.5, 22.1.

The data are in agreement with the literature.\(^{[55]}\)
6. Rotating Ring-Disk Electrode Experiments

Here, a more detailed discussion of the RRDE experiments is included. The discussion is started with measurements of the base electrolyte (2 mM Cp₂TiCl₂ and 0.2 M NBu₄PF₆ (TBAPF₆) in THF) and will continue with L1, L3 and L2 according to the increasing complexity of the systems.

6.1 General Remarks

In cyclic voltammetry, mass transport is only given by diffusion. This is why detected currents for an electron transfer event run through a peak value at a potential, where the concentration of the analyte at the surface is close to zero and the flux of species towards the electrode is at maximum. The following decrease of current density is a result of the diffusion layer extending into the bulk electrolyte, which leads to a decreasing concentration gradient. With a rotating electrode like a rotating disk or ring-disk electrode a continuous flow carries fresh bulk solution in vertical direction toward the electrode surface. However, close to the surface, the velocity of the electrolyte moving orthogonal to the electrode decreases to zero and changes into a radial flux due to the rotation of the electrode. Thus, a thin layer of electrolyte with a constant thickness is established in front of the electrode, through which the analyte has to diffuse. At the boundary to the bulk solution, the analyte concentration always equals the bulk concentration. As a consequence, a plateau rather than a peak is observed in a CV experiment at an RRDE once the concentration of the analyte at the surface of the electrode is close to zero. This is the diffusion limited current \( I_{\text{lim}} \). In a four-electrode set-up, with a disk and a ring electrode around it, the species formed in the original redox event at the disk or in a fast follow-up reaction are transported to the ring and can be detected. By adjusting the constant potential at the ring electrode, different species can be discerned. This feature of the RRDE makes the method perfectly suitable for our aim to analyze the different species already observed in CV measurements. All measurements were conducted at a sweep rate of 25 mV s⁻¹ with a reductive sweep followed by an oxidative back-sweep. Each measurement was performed at four rotation frequencies \( f \) (4, 9, 16 and 25 Hz). A thin-gap glassy carbon disk and ring (AFE7R9GCGC, Pine Research) with a disk surface area of \( A_{\text{Disk}} = 0.247 \text{ cm}^2 \) and a theoretical collection efficiency of \( N_0 = 0.37 \) was used as the working electrode. In order to put our later results into relation, we started with a measurement of Cp₂TiCl₂ in 0.2 M NBu₄PF₆/THF, which is the base electrolyte. This system was already studied in depth in the Daasbjerg group. The ring potential was set to 0.05 and 0.66 V vs. Ag/Ag⁺. The voltammograms are shown in Figure S3. Note that the disk potential has been iR-corrected. The uncompensated resistance was determined via electrochemical impedance spectroscopy and was in the range of 500 \( \Omega \). Note that the iR-correction does not severely influence the evaluation of the equilibrium constants as the constants are evaluated from diffusion-limited currents and transfer ratios.
According to the $E_{q}C_{r}$ mechanism, the reduced titanocene $[\text{Cp}_2\text{Ti(III)}\text{Cl}_2]^- \text{Cl}^-$ is in an equilibrium with $[\text{Cp}_2\text{Ti(III)}\text{Cl}]$ and $\text{Cl}^- (K_2^*, (1))$.

$$[\text{Cp}_2\text{Ti(III)}\text{Cl}_2]^- \text{Cl}^\ominus \rightleftharpoons K_{2^*} [\text{Cp}_2\text{Ti(III)}\text{Cl}] + \text{Cl}^\ominus \quad (1)$$

From the change of the coordination number at Ti results a significant difference of the redoxpotential of the two species. At a ring potential of 0.05 V only $[\text{Cp}_2\text{Ti(III)}\text{Cl}_2]^-$, directly formed in the electron transfer event at the disk electrode, can be detected at the ring. The cleaving product of the reversible follow up reaction, $[\text{Cp}_2\text{Ti(III)}\text{Cl}]$, is only detected at 0.66 V (see the CVs in section 3.3). Therefore, the ratio of ring and disk currents $I_R/I_D$ is higher at 0.66 V than at 0.05 V as both Ti(III) species are detected at the higher potential. Not all reduction products formed at the disk reach the ring electrode and can be detected. A part of the products diffuses into the bulk solution instead. The fraction that is detected at the ring electrode is a number specific for the ring-disk electrode and is called theoretical collection efficiency ($N_0$). If $I_R/I_D$ is normalized by $N_0$, the transfer ratio is obtained. At 0.66 V all species are reoxidized and $I_R/I_D/N_0$ should be equal to 1. The transfer ratios of the $\text{Cp}_2\text{TiCl}_2$ solution are depicted in Figure S4.
Figure S4. Transfer ratios $I_R/I_D/N_0$ of 2 mM Cp$_2$TiCl$_2$ in 0.2 M TBAPF$_6$/THF.

The transfer ratios recorded at 25 Hz (0.845 at 0.05 V and 1.068 at 0.66 V) give access to the dissociation equilibrium $K_2^*$ of [Cp$_2$Ti(III)Cl]$_2^-$ to form [Cp$_2$Ti(III)Cl] and Cl$^-$. At 0.05 V the concentration of [Cp$_2$Ti(III)Cl]$_2^-$ can directly be obtained by multiplication of the initial Ti concentration with the transfer ratio given that the rate constant of the dissociation-association equilibrium is small as compared to the residence time of the species at the ring electrode. Otherwise, additional [Cp$_2$Ti(III)Cl]$_2^-$ would be generated from the association reaction between [Cp$_2$Ti(III)Cl] and Cl$^-$. Therefore the measurement at 25 Hz was used for evaluation, where the transport of the species over the ring is the fastest. Alternatively, the transfer ratio could be extrapolated to an infinite rotation rate (e.g. vs. $f^{-1}$) to minimize the effect of the association reaction. However, due to experimental uncertainty as well as the lack of a suitable model for fitting, the extrapolation to infinite rotation rate would also pose a large uncertainty on final concentration. Having determined the concentration of [Cp$_2$Ti(III)Cl]$_2^-$, the concentration of [Cp$_2$Ti(III)Cl] can be extracted from the transfer ratio at 0.66 V. At 0.66 V both species can be oxidized and thus, the transfer ratio corresponds to the sum of the concentrations of [Cp$_2$Ti(III)Cl] and [Cp$_2$Ti(III)Cl]$_2^-$.

The ratio of both species is given by (2). $K_2^*$ in the base electrolyte amounts to 0.11 mM.

$$\frac{c([\text{Cp}_2\text{Ti(III)Cl}_2^-])}{c([\text{Cp}_2\text{Ti(II)Cl}])} = \frac{N(0.05 \text{V})}{N(0.66 \text{V}) - N(0.05 \text{V})}$$ (2)
6.2 Thiourea L1

In the CVs of titanocene dichloride and thiourea L1 a total of five species were observed. The Ti(IV) species [Cp₂Ti(IV)Cl₂] and [Cp₂Ti(IV)Cl₂]*L1 are detected on the reductive sweep and the Ti(III) species [Cp₂Ti(III)Cl₂]⁺, [Cp₂Ti(III)Cl₃]*L1 and [Cp₂Ti(III)Cl] are detected on the reverse sweep. For these species several equilibrium reactions have to be considered:

\[
[Cp₂Ti(IV)Cl₂] + L1 \rightleftharpoons K_a [Cp₂Ti(IV)Cl₂]^*L1 \tag{3}
\]

\[
[Cp₂Ti(III)Cl₂]⁺ + L1 \rightleftharpoons K_1 [Cp₂Ti(III)Cl₂]^*L1 \tag{4}
\]

\[
[Cp₂Ti(III)Cl₃]^*L1 \rightleftharpoons K_2 [Cp₂Ti(III)Cl] + Cl^*L1 \tag{5}
\]

Measurements at the RRDE of titanocene dichloride and different amounts of L1 were performed in 0.2 M TBAPF₆/THF to determine the relative and absolute amounts of each species. The voltammograms of the 4 and 25 Hz measurements and the corresponding transfer ratios at 0.05, 0.30 and 0.55 V ring potential are depicted in Figures S5 and S6.

**Figure S5**: Disk current densities i₀ (a), normalized ring currents iₖ/i₀ (b) and transfer ratios iₖ/i₅/i₀ (c) of the RRDE measurements of a solution of 2 mM Cp₂TiCl₂ in 0.2 M TBAPF₆/THF with different concentrations of L1 at a ring potential of 0.05 (I), 0.30 (II) and 0.55 V (III) and a rotation frequency f of 4 Hz.
The change of concentration of the analyte, the angular rotation frequency \( \nu \) and the bulk concentration of the analyte (Levich equation)\cite{510}

\[
i_{\text{lim,c}} = -0.62nFAD_0^{2/3} \omega^{1/2}v^{-1/6}c_0^*.
\]  

The other symbols have the usual meaning. The change of \( i_{\text{lim}} \) is an indication for the formation of a new species with a smaller diffusion coefficient, which is the \([\text{Cp}_2\text{Ti(IV)Cl}_2]^*\text{L1}\) adduct. The gradual change of \( i_{\text{lim}} \) can be explained with the reversibility of the adduct formation (3). On its path to the disk electrode surface \([\text{Cp}_2\text{Ti(IV)Cl}_2]\) can associate to \( \text{L1} \) and dissociate again. The higher the concentration of \( \text{L1} \), the larger is the diffusion length in the associated species. As a consequence, the...
diffusion of [Cp₂Ti(IV)Cl₂]*L₁ is best reflected in the measurement with 10 mM of L₁. In Figure S7 the diffusion limited currents at the disk for Cp₂TiCl₂ and with 10 mM and with 1 mM L₁ (here the shoulder current was taken) are plotted against the square root of the rotation frequency.

![Figure S7. Diffusion limited current densities at the disk i₀ as a function of f^{1/2} for Cp₂TiCl₂ and with 10 mM of L₁ or 1 mM of L₁ (shoulder current). The slopes of the linear fits are given as m.](image)

From the slopes m of a linear fit the ratio of the diffusion coefficients of [Cp₂Ti(IV)Cl₂] and [Cp₂Ti(IV)Cl₂]*L₁ can be obtained using (6). This ratio amounts to 1.15:

\[
\frac{D([Cp₂Ti(IV)Cl₂])}{D([Cp₂Ti(IV)Cl₂]+L₁)} = \left( \frac{m_{\text{Diff}}([Cp₂Ti(IV)Cl₂])}{m_{\text{Diff}}([Cp₂Ti(IV)Cl₂]+L₁)} \right)^{3/2}
\]

(7)

The diffusion coefficient D([Cp₂Ti(IV)Cl₂]) for our system is not known in the literature. However, it can be easily calculated from the slope in Figure S7 (blue trace), if the kinematic viscosity ν is known. Since ν scales to the power of −1/6 (see (6)) it is acceptable to approximate this value by using ν(THF) without conducting salt. From the literature a value of 5.2×10⁻³ cm² s⁻¹ is obtained. Thus, 8.8×10⁻⁶ cm² s⁻¹ results for D([Cp₂Ti(IV)Cl₂]) and 7.6×10⁻⁶ cm² s⁻¹ for D([Cp₂Ti(IV)Cl₂]*L₁). The diffusion coefficient ratio together with the slopes of the base electrolyte and of the linear fit of the shoulder currents can be used to determine the equilibrium constant of association for (3) as the current – and as a result the slope m – in the shoulder is proportional to the concentration of the adduct in this equilibrium. The following relation is obtained:

\[
\frac{c₀(Cp₂TiCl₂)}{c_{\text{eq}}([Cp₂Ti(IV)Cl₂]+L₁)} = \frac{m_{\text{Diff}}([Cp₂Ti(IV)Cl₂]+L₁)}{m_{\text{shoulder}}([Cp₂Ti(IV)Cl₂]+L₁)}
\]

(8)

Here, c₀ denotes the initial concentration of Cp₂TiCl₂. Kₐ then amounts to 0.69 mM⁻¹.
The ring potential for the measurements with Cp₂TiCl₂ and L1 was set to 0.05, 0.30 and 0.55 V vs. Ag/Ag⁺. Analogous to before, the detection of [Cp₂Ti(III)Cl₂]⁺, [Cp₂Ti(III)Cl₂]⁺*L1 and [Cp₂Ti(III)Cl] was achieved step-wise. The transfer ratios as a function of the concentration of L1 are given in Figure S8.

![Figure S8](image)

**Figure S8.** Transfer ratios \( I_R/I_D/N_0 \) for the measurements of Cp₂TiCl₂ and L1 at different concentrations of L1 at ring potentials of 0.05, 0.30 and 0.55 V and at a rotation frequency \( f = 25 \) Hz.

The transfer ratios yield the ratios of the equilibrium concentrations for equations (4) and (5).

\[
\frac{c([\text{Cp}_2\text{Ti}(\text{III})\text{Cl}_2]^+)}{c([\text{Cp}_2\text{Ti}(\text{III})\text{Cl}_2]^+*\text{L1})} = \frac{N(0.05 \text{ V})}{N(0.30 \text{ V}) - N(0.05 \text{ V})} \tag{9}
\]

\[
\frac{c([\text{Cp}_2\text{Ti}(\text{III})\text{Cl}_2]^+*\text{L1})}{c([\text{Cp}_2\text{Ti}(\text{III})\text{Cl}_2]^+)} = \frac{N(0.30 \text{ V}) - N(0.05 \text{ V})}{N(0.5 \text{ V}) - N(0.30 \text{ V}) - N(0.05 \text{ V})} \tag{10}
\]

For the association of L1 to the anionic Ti(III) species \( K_1 \) amounts to 2 mM⁻¹ and for the cleaving of Cl⁻ *L1 off Cp₂TiCl₂ *L1 \( K_2 \) equals 2.8 mM.

The observed gradual shift in the reduction potential with increasing amount of L1 gives insight into the overall mechanics of the equilibria in both oxidation states of Ti. It implies that the Nernst equation\(^{[512]} \) for this redox process depends on the concentration of free thiourea.

\[
E = E_0 - \frac{RT}{F} \ln c(L1)^p - \frac{RT}{F} \ln \left( K' \frac{c([\text{Cp}_2\text{Ti}(\text{III})\text{Cl}_2]^+*\text{L1}_p)}{c([\text{Cp}_2\text{Ti}(\text{IV})\text{Cl}_2]^+*\text{L1}_p)} \right) \tag{11}
\]

\( K' \) is introduced as a constant factor to account for the complex mesh of equilibria. A plot (see Figure S9) of the half-wave potential \( E_{1/2} \) as a function of the decadic logarithm of c(L1) shows a slope of roughly 60 mV dec⁻¹ at all rotation frequencies.
Therefore, $p$ in (11) must be equal to 1, which is indicative of 1:1 complexation between L1 and the titanocene species. With all experimental findings in mind we propose the electrochemical mesh-scheme shown in Scheme S1 for the Cp₂TiCl₂/L1 couple.

\[
\begin{align*}
[Cp_2Ti(IV)Cl_2] & \xrightleftharpoons{L1} [Cp_2Ti(IV)Cl_2]^*L1 \\
[Cp_2Ti(III)Cl_2] & \xrightleftharpoons{L1} [Cp_2Ti(III)Cl_2]^*L1 \\
[Cp_2Ti(III)Cl] + Cl^- & \xrightleftharpoons{L1} [Cp_2Ti(III)Cl] + Cl^*L1
\end{align*}
\]

**Scheme S1.** Electrochemical mesh-scheme for the redox system of Cp₂TiCl₂ in the presence of L1.

It considers the $E_qC_r$ mechanism of titanocene dichloride and adds the L1 containing species. With the equilibrium constants we can quantify how effectively the $C_r$ reaction (cleaving off of ‘Cl’–) is amplified in the presence of L1 by comparing $K_2$ to $K_2^*$. This gives a factor of 25.
6.3 Sulfonamide L3

In contrast to thiourea L1 the sulfonamide L3 shows a double peak in the oxidation wave of ‘Cp₂TiCl’.

This lead us to assume the presence of an adduct between the active species and L3, [Cp₂Ti(III)Cl]⁺L3. Thus, the following equilibrium reactions have to be considered:

\[
[Cp₂Ti(IV)Cl₂] + L3 \xrightleftharpoons[Kₐ]{\text{Kₐ}} [Cp₂Ti(IV)Cl₂]⁺L3 \quad (12)
\]

\[
[Cp₂Ti(III)Cl₂] \xrightarrow[K₁]{\text{K₁}} [Cp₂Ti(III)Cl₂]⁺L₃⁻ \quad (13)
\]

\[
[Cp₂Ti(III)Cl₂]⁺L₃⁻ \xrightleftharpoons[K₂]{\text{K₂}} [Cp₂Ti(III)Cl] + Cl⁻L₃⁻ \quad (14)
\]

\[
[Cp₂Ti(III)Cl] + L3 \xrightleftharpoons[K₃]{\text{K₃}} [Cp₂Ti(III)Cl]⁺L₃ \quad (15)
\]

RRDE measurements with Cp₂TiCl₂ and L3 were performed in the same manner as described for L1. The voltammograms of the 4 and 25 Hz measurements and the corresponding transfer ratios at 0.05, 0.23, 0.42 and 0.66 V ring potential are depicted in Figures S10 and S11.

![Figure S10](image-url)

**Figure S10**: Disk current densities \(i_D\) (a), normalized ring currents \(i_R/N_D\) (b) and transfer ratios \(i_D/i_R/N_D\) (c) of the RRDE measurements of a solution of 2 mM Cp₂TiCl₂ in 0.2 M TBAPF₆/THF with different concentrations of L3 at a ring potential of 0.05 (I), 0.23 (II), 0.42 (III) and 0.66 V (IV) and a rotation frequency \(f\) of 4 Hz.
Figure S11: Disk current densities $i_0$ (a), normalized ring currents $I_R/N_0$ (b) and transfer ratios $I_R/I_D/N_0$ (c) of the RRDE measurements of a solution of 2 mM Cp$_2$TiCl$_2$ in 0.2 M TBAPF$_6$/THF with different concentrations of L3 at a ring potential of 0.05 (I), 0.23 (II), 0.42 (III) and 0.66 V (IV) and a rotation frequency $f$ of 25 Hz.

Here, the same general observations can be made from the voltammograms at the disk as for L1. The current density $i_0$ in the diffusion limited region is decreasing in value with increasing amount of L3, a shoulder at substoichiometric amounts of L3 indicates the formation of the [Cp$_2$Ti(Iv)Cl$_2$]*L3 adduct and a gradually shifting reduction potential with increasing concentration of L3 is apparent. The diffusion limited current densities $i_0$ of the base electrolyte containing Cp$_2$TiCl$_2$ and after addition of 10 mM of L3 and the shoulder currents of the measurements with 1 mM of L3 are plotted against $f^{1/2}$ in Figure S12.
Diffusion limited current densities at the disk $i_0$ as a function of $f^{1/2}$ for Cp$_2$TiCl$_2$ and with 10 mM of L3 or 1 mM of L3 (shoulder current). The slopes of the linear fits are given as $m$.

Using (7) the ratio of the diffusion coefficients of [Cp$_2$Ti(IV)Cl$_2$] and its adduct with L3 can be calculated to 1.15. Thus, 7.6×10$^{-6}$ cm$^2$ s$^{-1}$ results for $D([Cp_2Ti(IV)Cl_2]*L3)$. Accordingly, the equilibrium constant for (12), $K_a$, amounts to 1.07 mM$^{-1}$ (compare (8)).

By setting the ring potential for the measurements to 0.05, 0.23, 0.42 and 0.66 V, all Ti(III) species could be detected as in the previous cases. The transfer ratios as a function of the concentration of L3 are given in Figure S13.

Transfer ratios $I_R/I_D/N_0$ for the measurements of Cp$_2$TiCl$_2$ and L3 at different concentrations of L3 at ring potentials of 0.05, 0.23, 0.42 and 0.66 V and at a rotation frequency $f$ of 25 Hz.
The transfer ratios yield the equilibrium constants for (13) to (15) by following the same procedure as for L1 (compare (9) and (10)). The adduct species [Cp₂Ti(III)Cl]L₃ is detected before [Cp₂Ti(III)Cl]⁻. This results from the binding mode revealed in the DFT calculations. For the association of L₃ to [Cp₂Ti(III)Cl]⁻, K₁ amounts to 0.4 mM⁻¹ and for the cleaving of Cl⁻L₃ off Cp₂TiCl₂⁺L₃, K₂ equals 3.0 mM. The formation of the [Cp₂Ti(III)Cl]·L₃ adduct has an equilibrium constant K₃ of 0.7 mM⁻¹.

A plot (see Figure S14) of the half-wave potentials E₁/₂ of the disk voltammograms as a function of the decadic logarithm of c(L₃) yields a slope of 60 mV dec⁻¹.

![Plot](image)

**Figure S14.** Plot of the half-wave potential E₁/₂ of the RRDE measurements with Cp₂TiCl₂ and L₃.

This implies a 1:1 complex formation for the Cp₂TiCl₂/L₃ couple as for L1 before. We propose the electrochemical mesh-scheme shown in Scheme S2 for the Cp₂TiCl₂/L₃ couple.

\[
\begin{align*}
[Cp₂Ti(IV)Cl₂] & \xrightarrow{L₃} [Cp₂Ti(IV)Cl₂]⁺L₃ & K₂ = 1.07 \text{ mM}⁻¹ \\
[Cp₂Ti(III)Cl₂]⁻ & \xrightarrow{L₃} [Cp₂Ti(III)Cl₂]⁺L₃ & K₁ = 0.4 \text{ mM}⁻¹ \\
[Cp₂Ti(III)Cl] + Cl⁻ & \xrightarrow{L₃} [Cp₂Ti(III)Cl]⁺Cl⁻ & K₃ = 0.7 \text{ mM}⁻¹ \\
\end{align*}
\]

**Scheme S2.** Electrochemical mesh-scheme for the redox system of Cp₂TiCl₂ in the presence of L₃.

The mesh-scheme with L₃ looks very similar to the one for L1. Only the occurrence of [Cp₂Ti(III)Cl]⁺L₃ makes an addition to the scheme necessary. According to the equilibrium constants K₂ and K₂⁺, the C₃...
reaction is amplified by a factor of 27 in the presence of L3. This is comparable to L1. However, the access to [Cp₂Ti(III)Cl]⁺L3 increases the extent of the C₁ reaction further.

6.4 Squaramide L2

Squaramide L2 similar to L3 exhibits a complicated oxidation wave in the range of the neutral Ti(III) with at least two oxidation peaks. Therefore we considered the same equilibrium reactions as we did for L3:

\[
\begin{align*}
[Cp₂Ti(IV)]⁺L₂ & \xrightleftharpoons[K_a^\text{-1}]{K_a} \text{[Cp₂Ti(IV)]}^*L₂ \\
[Cp₂Ti(III)]⁺L₂ & \xrightleftharpoons[K_i, K_i']{K_i} \text{[Cp₂Ti(III)]}^*L₂ \\
[Cp₂Ti(III)]⁺L₂^* & \xrightleftharpoons[K_2]{K_2} \text{[Cp₂Ti(III)]} + \text{Cl}^*L₂ \\
[Cp₂Ti(III)]⁺ + L₂ & \xrightleftharpoons[K_3]{K_3} \text{[Cp₂Ti(III)]}^*L₂
\end{align*}
\]

The voltammograms of the 4 and 25 Hz measurements and the corresponding transfer ratios at 0.05, 0.23, 0.42 and 0.72 V ring potential are depicted in Figures S15 and S16.

![Volammograms and transfer ratios](image)

**Figure S15**: Disk current densities i₀ (a), normalized ring currents iₐ/iₐ₀ (b) and transfer ratios iₐ/i₀/iₐ₀ (c) of the RRDE measurements of a solution of 2 mM Cp₂TiCl₂ in 0.2 M TBAPF₆/THF with different concentrations of L2 at a ring potential of 0.05 (i), 0.23 (ii), 0.42 (iii) and 0.72 V (iv) and a rotation frequency f of 4 Hz.
Figure S16: Disk current densities $i_D$ (a), normalized ring currents $i_R/N_0$ (b) and transfer ratios $i_D/i_R/N_0$ (c) of the RRDE measurements of a solution of 2 mM Cp$_2$TiCl$_2$ in 0.2 M TBAPF$_6$/THF with different concentrations of L2 at a ring potential of 0.05 (i), 0.23 (ii), 0.42 (iii) and 0.72 V (iv) and a rotation frequency $f$ of 25 Hz.

The diffusion limited current densities $i_D$ of the base electrolyte containing Cp$_2$TiCl$_2$ and after addition of 10 mM of L2 and the shoulder currents of the measurements with 1 mM of L2 are plotted against $f^{1/2}$ in Figure S17.

Figure S17. Diffusion limited current densities at the disk $i_D$ as a function of $f^{1/2}$ for Cp$_2$TiCl$_2$ and with 10 mM of L2 or 1 mM of L2 (shoulder current). The slopes of the linear fits are given as $m$. 
Using (7) the ratio of the diffusion coefficients of \([\text{Cp}_2\text{Ti(IV)}\text{Cl}_2]\) and its adduct with \(\text{L}_2\) can be calculated to 1.33. Thus, \(6.6\times10^{-6} \text{ cm}^2 \text{ s}^{-1}\) results for \(D([\text{Cp}_2\text{Ti(IV)}\text{Cl}_2]^*\text{L}_2)\). Accordingly, the equilibrium constant for (16), \(K_a\), amounts to 1.81 mm\(^{-1}\).

By setting the ring potential for the measurements to 0.05, 0.23, 0.42 and 0.72 V, all Ti(III) species could be detected. The transfer ratios as a function of the concentration of \(\text{L}_2\) are given in Figure S18.

\[
\text{Figure S18. Transfer ratios } I_R/I_D/N_0 \text{ for the measurements of } \text{Cp}_2\text{TiCl}_2 \text{ and } \text{L}_2 \text{ at different concentrations of } \text{L}_2 \text{ at ring potentials of 0.05, 0.23, 0.42 and 0.72 V and at a rotation frequency } f \text{ of 25 Hz.}
\]

The transfer ratios yield the equilibrium constants for (17)–(19). For the association of \(\text{L}_2\) to \([\text{Cp}_2\text{Ti(III)}\text{Cl}_2]^*\) \(K_1\) amounts to 0.3 mm\(^{-1}\) and for the cleaving of \(\text{Cl}^*\text{L}_2\) off \([\text{Cp}_2\text{Ti(III)}\text{Cl}_2]^*\text{L}_2\) \(K_2\) equals 54 mm. The formation of the \([\text{Cp}_2\text{Ti(III)}\text{Cl}]^*\text{L}_2\) adduct has an equilibrium constant \(K_3\) of 0.5 mm\(^{-1}\).
A plot (see Figure S19) of the half-wave potentials $E_{1/2}$ of the disk voltammograms yields a slope of 30 mV dec$^{-1}$ for L2.

![Graph](image)

**Figure S16.** Plot of the half-wave potential $E_{1/2}$ of the RRDE measurements with Cp$_2$TiCl$_2$ and L2.

The smaller slope in the plot must originate from a different Nernst equation. Here the redox potential is proportional to $\log(c(L2)/mM)$ with $q = \rho/2$ (compare (11)). This can be explained with a 2:1 complexation of [Cp$_2$Ti(III)Cl] with L2 as shown in reaction (20):

$$2 \text{[Cp}_2\text{Ti(III)Cl]} + \text{L2} \overset{K_3'}{\longrightarrow} \text{([Cp}_2\text{Ti(III)Cl]_2^*L2}$$  \hspace{1cm} (20)

Here, two molecules of [Cp$_2$Ti(III)Cl] are bound to a single molecule of L2, resulting in a 2:1 complexation. This result was validated by the DFT calculations. Evaluation of the transfer ratios considering (20) instead of (19), different values for $K_3'$ (0.2 mM$^{-1}$) and $K_3$ (0.1 mM$^{-2}$) are obtained. $K_2$ remains unchanged. In reality, the equilibria from (19) and (20) are likely to be present side by side. The given numbers for $K_3^{(i)}$ and $K_3^{(j)}$ can therefore only be considered as a simplification. We propose the electrochemical mesh-scheme shown in Scheme S3 for the Cp$_2$TiCl$_2$/L2 couple.
**Scheme S3.** Electrochemical mesh-scheme for the redox system of Cp₂TiCl₂ in the presence of L₂.

The mesh-scheme with L₂ looks very similar to the one for L₃. However it adds the formation of the 2:1 adduct. According to the equilibrium constants the Cᵣ reaction is amplified by a factor of 491 in the presence of L₂. The access to [Cp₂Ti(III)Cl]⁺L₂ and ([Cp₂Ti(III)Cl])₂⁺L₂ increases the extent of the Cᵣ reaction even more.

### 6.5 Comparison

In order to easily compare the solutions of Cp₂TiCl₂ with L₁ – L₃ it is helpful to calculate the solution composition of the discussed titanocene species in %. Table S1 shows the compositions before and after reduction for a 1:1 mixture of 2 mM Cp₂TiCl₂ and each additive. For L₂, (20) is not considered here.

**Table S1.** Solution compositions of titanocene species before (left) and after reduction (right) for 2 mM Cp₂TiCl₂ and with the additives L₁ – L₃ in a 1:1 mixture in %.

|                  | [Cp₂Ti(IV)Cl₂] | [Cp₂Ti(IV)Cl₂]⁺L | [Cp₂Ti(III)Cl]⁻ | [Cp₂Ti(III)Cl]⁺L | [Cp₂Ti(III)Cl]⁻ *L | [Cp₂Ti(III)Cl]⁺L |
|------------------|----------------|------------------|-----------------|-----------------|-------------------|-----------------|
| no L             | 100            |      —          | 79              |      —          | 21                |      —          |
| L₁               | 56             | 44               | 14              | 28              | 58                | 0               |
| L₂               | 40             | 60               | 19              | 4               | 60                | 17              |
| L₃               | 49             | 51               | 32              | 12              | 25                | 31              |

From these values a trend in the receptor ability of the additives can be derived. The binding to [Cp₂Ti(IV)Cl₂] decreases in the order Z > X > Y. However, [Cp₂Ti(IV)Cl₂] and [Cp₂Ti(IV)Cl₂]⁺L are present in the solution in similar amounts in all three cases. All additives can effectively reduce the amount of anionic titanocene in the reduced solutions and increase the amount of active catalyst. The total amount of neutral Ti(III) complexes is however largest for L₂, followed by L₁ and L₃.
7. Density Functional Theory Calculations

7.1 General Information

All visualizations of structures were created with UCSF Chimera\textsuperscript{[S13]} 1.14.0. We used the xTB,\textsuperscript{[S14]} CREST\textsuperscript{[S15]} and ENSO\textsuperscript{[S16]} programs to determine the structures with the lowest free energy in THF solution for each ligand L and all complexes. These calculations were conducted in the same workflow. Manually prepared starting structures, which are initially pre-optimized with the GFN2-\textit{xTB}[GBSA] tight binding model, are used in the CREST program that employs MTD at the same level in order to obtain a relative complete ensemble of likely structures. The ENSO program determines the equilibrium (Boltzmann) populations for a few low-lying conformers at higher theoretical levels in three steps using TURBOMOLE.\textsuperscript{[S17]}

First, already relatively accurate B97-3c[DCOSMO-RS(THF)] (a composite low-cost DFT method\textsuperscript{[S18]}), single point energies are calculated on the CREST ensemble. Structures within an energy threshold of 4 kcal mol\textsuperscript{-1} above the lowest lying structure are then fully optimized at the same level. In this first filtering step thermostatistical free energies in the modified rigid-rotor/harmonic-oscillator (mRRHO) approximation\textsuperscript{[S19]} calculated with GFN2-\textit{xTB}[GBSA] and the free energy of solvation in THF calculated with the accurate COSMO-RS\textsuperscript{[S20]} solvation model are added. Finally, for all structures within a 2 kcal mol\textsuperscript{-1} threshold an even better single point energy is computed at the PW6B95-D3/def2-TZVPP\textsuperscript{[S21]} hybrid DFT level which basically replaces the corresponding B97-3c energy. In summary, the final complete total free energy used consists of the mRRHO part from the GFN2-\textit{xTB} treatment, the COSMO-RS part in THF for solvation and the basic electronic energy with the PW6B95-D3 functional. In the following, the conformer of each species with the lowest total free energy is given, if not stated otherwise.
7.2 Calculated Structures

The basic receptor ability of the discussed additives can already give useful information for later analysis. The calculated structures of the H-bond donors L1, L2 and L3 are given in Figure S17. These conformers are the minimum structures in the electric field of a capacitor resembling the \( \varepsilon_r \) of THF.

Figure S17. Minimum structures of the H-bond donors L1, L2 and L3 obtained from DFT calculations. The energetic differences (\( \Delta G_{298.15} \)) to the next higher lying conformers are given in kcal mol\(^{-1}\). The number shown for L2 is the energy difference to the respective conformer in the first optimization step (\( E_{el} \)) as no conformer was within the threshold.

L1 shows a preferred orientation that allows H-bonding to a single H-bond acceptor with both N-H groups. In contrast, the N-H groups in L2 and L3 point into different directions. In order to properly discuss the reaction energies of the adduct formations, the binding affinity of the anion receptors to solvent molecules has to be assessed. The corresponding structure optimizations can be considered as a first approximation to explicit solvation. The direct anion receptor ability of each additive can be estimated by complexation with a simple anionic species. The Cl\(^-\) anion is a natural choice in the context of our investigations. Therefore, expanding on the details given in the manuscript the supramolecular complexes of the receptors with THF and Cl\(^-\) are depicted in Figure S18.
The calculations reveal L2 as the best H-bond donor. It binds to the oxygen atom of THF with both N—H groups. L1 and L3 only form a single H-bond. This observation emphasizes the weak dipole in the THF molecule. In the Cl*L complexes a dramatic change is evident. All receptors bind with both N—H groups. This reflects the association free enthalpies, which are much more strongly binding for Cl* than for THF.

The calculations of the [Cp₂Ti(IV)Cl₂]L2 adduct revealed a van der Waals complex as lowest energy structure. It does not align with the experimental observations but is depicted in Figure S19 for reference.

For the adduct formation between [Cp₂Ti(III)Cl] and L calculations without and with a molecule of THF binding to the free coordination site of Ti come to distinctly different results. The important
aspects have been highlighted in the manuscript. In Figure S20 we show the full set of calculated structures.

**Figure S20.** Calculated structures of the $[\text{Cp}_2\text{Ti(III)Cl}]^*\text{L}$ (left) and $[\text{Cp}_2\text{Ti(III)Cl}](\text{THF})^*\text{L}$ complexes (right). $\Delta G_{298.15}$ and $\Delta H_{298.15}$ are the Gibbs energy and reaction enthalpy of association for each adduct starting from $[\text{Cp}_2\text{Ti(III)Cl}]$, L (and THF).
Calculated structures of the 2:1 adducts between [Cp₂Ti(III)Cl] and L₂ without THF and with a single THF molecule are depicted in Figure S21. In both structures coordination of a carbonyl oxygen of L₂ to the Ti center can be observed. A calculation of (([Cp₂Ti(III)Cl])₂(THF))₃*L₂ resultet in a van der Waals complex, which would have to be considered as a 1:1 complex in the context of our investigations.

\[
\begin{align*}
\text{([Cp₂Ti(III)Cl])₂*L₂:} \\
\Delta G_{298.15} &= 8.2 \text{ kcal mol}^{-1} \\
\Delta H_{298.15} &= -2.8 \text{ kcal mol}^{-1}
\end{align*}
\]

\[
\begin{align*}
\text{([Cp₂Ti(III)Cl])₃(THF)*L₂:} \\
\Delta G_{298.15} &= 3.7 \text{ kcal mol}^{-1} \\
\Delta H_{298.15} &= -18.4 \text{ kcal mol}^{-1}
\end{align*}
\]

Figure S21. Calculated structures of the ([Cp₂Ti(III)Cl])₂*L₂ and ([Cp₂Ti(III)Cl])₃(THF)*L₂ complexes. ΔG_{298.15} and ΔH_{298.15} are the Gibbs energy and reaction enthalpy of association for each adduct starting from [Cp₂Ti(III)Cl], L (and THF).

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9. Structural Data (xyz-Format)

**L1 (Fig. S17, entry 1):**

| Atom | x     | y     | z     |
|------|-------|-------|-------|
| S    | 0.0049776 | 0.9609810 | 1.1164922 |
| C    | 0.0011123 | -0.3416911 | 0.0581255 |
| N    | 1.1283206 | -0.9608054 | -0.395179 |
| C    | 2.4638247 | -0.5788993 | -0.2376718 |
| C    | 2.8709839 | 0.7527421 | -0.2590131 |
| C    | 4.2202212 | 1.0565337 | -0.1440093 |
| C    | 5.1783814 | 0.0613812 | -0.0167888 |
| C    | 4.7601079 | -1.2632704 | -0.0258371 |
| C    | 3.4178437 | -1.5917486 | -0.1370008 |
| H    | 6.7115416 | -2.0953108 | 1.0342690 |
| H    | 6.2235500 | 0.3089187 | 0.0742372 |
| C    | 4.6459070 | 2.4959231 | -0.1103531 |
| F    | 4.6600743 | 2.9836379 | 1.1622576 |
| F    | 5.8923919 | 2.6812569 | -0.6072617 |
| F    | 3.8160339 | 3.2989927 | -0.820843 |
| H    | 2.1434965 | 1.5360708 | -0.3761643 |
| H    | 1.0080519 | -1.8628451 | -0.8379202 |
| N    | -1.1294014 | -0.9526808 | -0.4018930 |
| C    | -2.4644273 | -0.5708758 | -0.2366287 |
| C    | -3.4179960 | -1.5858351 | -0.1499800 |
| C    | -4.7606224 | -1.2607126 | -0.0375840 |
| C    | -5.1806965 | 0.0634295 | -0.0134243 |
| C    | -4.2230507 | 1.0606700 | -0.1261942 |
| C    | -2.8727829 | 0.7603118 | -0.2416428 |
| H    | -2.1455553 | 1.5457539 | -0.3457451 |
| C    | -4.6485903 | 2.4997211 | -0.0772052 |
| F    | -3.8315980 | 3.3061933 | -0.7984953 |
| F    | -5.9036845 | 2.6877961 | -0.550120 |
| F    | -4.6386979 | 2.9812781 | 1.1977796 |
| H    | -6.2266377 | 0.3068689 | 0.077037 |
| C    | -5.8018894 | -2.3391195 | 0.0278293 |
| F    | -6.5064427 | -2.4288122 | -1.1356596 |
| F    | -5.2794415 | -3.5662889 | 0.2580480 |
| F    | -6.7130268 | -2.1092212 | 1.0080375 |
| H    | -3.0971426 | -2.6160959 | -0.1597688 |
| H    | -1.0112183 | -1.8527319 | -0.8418510 |
L2 (Fig. S17, entry 2):

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|   |   |   |   |
|---|---|---|---|
| 0 | -5.7173392 | -1.6510425 | -0.0254025 |
| C | -4.8973227 | -0.7536750 | -0.0313184 |
| C | -3.4205576 | -0.6933968 | -0.0729465 |
| N | -2.5486540 | -1.6992215 | -0.2044017 |
| C | -1.2455006 | -1.6410191 | -0.7058255 |
| C | -0.8146707 | -0.5706297 | -1.4879820 |
| C | 0.4938997  | -0.5403300 | -1.9371858 |
| C | 1.3792859  | -1.5746026 | -1.6553201 |
| C | 0.9222818  | -2.6498404 | -0.9067434 |
| C | -0.3794759 | -2.6954829 | -0.4317259 |
| H | -0.7174429 | -3.5163858 | 0.1803655 |
| C | 1.3851869  | -3.8122351 | -0.6389447 |
| F | 3.1417886  | -3.4598180 | -0.6431815 |
| F | 1.5890899  | -4.031428 | 0.5542664 |
| F | 1.6917406  | -4.7828036 | -1.5868714 |
| H | 2.3965027  | -5.359336 | -2.0104487 |
| C | 0.9882406  | -0.6090901 | -2.7676882 |
| F | 0.6009280  | 1.5802395 | -2.9335927 |
| F | 1.3604367  | 0.2066357 | -4.0128263 |
| F | 2.0805158  | 1.1973999 | -2.2142782 |
| H | -1.4939907 | 0.2264583 | -1.7362326 |
| H | -2.9251556 | -2.6250554 | -0.0500724 |
| C | -3.4170470 | 0.7058454 | 0.0752762 |
| N | -2.5404040 | 1.7075859 | 0.2057950 |
| C | -1.2369057 | 1.6440005 | 0.7062047 |
| C | -0.3683668 | 2.6975431 | 0.4340090 |
| C | 0.9338268  | 2.6474595 | 0.9073697 |
| C | 1.3887086  | 1.5687883 | 1.6521232 |
| C | 0.5009614  | 0.5365285 | 1.9328926 |
| C | -0.8082626 | 0.5712005 | 1.4855716 |
| H | -1.4886490 | -0.2248909 | 1.7335887 |
| C | 0.9932039  | -0.6151352 | 2.7614552 |
| F | 0.6608569  | -1.5865751 | 2.9230146 |
| F | 2.0872154  | -1.2016375 | 2.2093330 |
| F | 1.3626326  | -0.2154245 | 4.0086603 |
| H | 2.4062933  | 1.5285807 | 2.0041938 |
| C | 1.8515233  | 3.8071744 | 0.6439078 |
| F | 1.5921356  | 4.4179281 | -0.5368400 |
| F | 3.1553372  | 3.4459512 | 0.6231755 |
| F | 1.7290360  | 4.7645438 | 1.6081275 |
| H | -0.7057359 | 3.5217045 | -0.1739804 |
| H | -2.9139702 | 2.6349728 | 0.0536237 |
| C | -4.8937286 | 0.7730245 | 0.0336664 |
| O | -5.7096598 | 1.6739813 | 0.0271205 |
### L3 (Fig. S17, entry 3):

|   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   | |
THF*L1 (Fig. S18, left entry 1):

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S  -1.2336927  -3.1945195  1.7473956
C  -0.2811730  -1.9542410  1.1354278
N  1.0778930  -2.0854470  1.1250669
C  2.0358777  -1.4294695  0.3473684
C  1.7472930  -0.8586341  -0.8948526
C  2.7631109  -0.2668348  -1.6261398
C  4.0738811  -0.2372512  -1.1619035
C  4.3506429  -0.8307603  0.0601363
C  3.3487226  -1.4190288  0.8177725
H  3.5689899  -1.8667868  1.7739872
C  5.7404293  -0.7676566  0.6238885
F  5.8825803  -1.8764837  1.3347068
F  6.0619143  -0.6234031  0.3310783
H  4.8522839  -0.2255826  1.7458512
C  2.4793874  0.3332214  -2.9735105
F  2.9293958  1.6129765  -3.0609861
F  1.1604738  0.3617733  -3.2757250
C  3.0936584  0.3568953  -3.9714667
H  0.7442524  -0.8872809  -1.2848207
N  -0.7382313  -0.7503569  0.7021568
C  -2.0582672  -0.3910473  0.4303667
C  -2.9549402  -1.2571501  -0.1898581
C  -4.2404849  -0.8180416  -0.4720678
C  -4.6528986  -0.4699961  -0.1598019
C  -3.7385420  1.3308552  0.4335993
C  -2.4529661  0.9114664  0.7337810
H  -1.7471327  1.5806827  1.2007724
C  -4.1852988  2.7203072  0.7787379
F  -5.1208434  2.7179175  1.7668618
F  -4.7542594  3.3506314  -0.2830478
F  -3.1714612  3.5906082  1.2042761
H  -5.6535950  0.8005815  -0.3861544
C  -5.2215659  -1.7752950  -1.0850737
F  -6.1593246  -1.1497855  -1.8367916
F  -5.8955760  -2.4771400  -0.1310607
F  -4.6238437  -2.6915423  -1.8851675
H  -2.6438726  -2.2520480  -0.4556554
H  -0.0958020  0.0419992  0.8191901
O  0.7537186  1.5631821  1.3098852
C  1.2591827  2.5250359  0.3565442
C  2.6694884  2.8450750  0.8074177
H  3.3686667  2.1095788  0.4114690
H  2.9925696  3.8322178  0.4850008
C  2.5578125  2.7134755  2.3226490
C  2.1204056  3.6152633  2.7510883
H  3.5145214  2.5361856  2.0082180
C  1.6103348  1.5381045  2.4778101
THF*L2 (Fig. S18, left entry 2):

H     0.9802223    1.5975823    3.3633070
H     2.1483478    0.5881568    2.4911714
H     0.6176495    3.4090304    0.3789548
H     1.2056609    2.0784821 -0.6336194

THF*L2 (Fig. S18, left entry 2):

H     1.0981758    0.6646117 -0.0006273
N     1.5410682 -0.2601477    0.0051092
C     0.7006365 -1.3025641    0.0071256
C     -0.71039     -1.3009716    0.0158199
N     -1.5484910 -0.2566670    0.0255902
C     -2.9412024 -0.2318887    0.0192949
C     -3.7324648 -1.3740817    0.0033421
N     -4.9265810    1.1299483    0.0201522
C     -5.4996667    1.0270957    0.0297100
N     -2.9367803    1.9156816    0.0428547
C     -5.5906482    2.4764709    0.0260707
F     -6.3781785    2.6442606    1.1197771
F     -4.7037238    3.5003199    0.0214583
F     -6.3925533    2.6465087  -1.0564989
N     -6.8063040    0.0858965  -0.0014696
C     -5.9325843 -2.5072858  -0.0120974
F     -7.2629754 -2.2753817  -0.0102206
F     -5.6639693  -3.2632821  -1.1092932
F     -5.650149    -3.2876614    1.0679215
H     -3.2747910 -2.3534225    0.0052297
H     -1.1040078    0.6672005    0.0321724
C     -0.7658389  -2.7798512    0.0103628
O     -1.6234968 -3.6446809    0.0114089
C     0.7527758  -2.7815466    0.0032067
O     1.6085270  -3.6482543  -0.0033345
C     2.9337933  -0.2384832    0.0031100
C     3.7226520  -1.3824214  -0.0008927
C     5.1064554  -1.2561430    0.0001516
C     5.7260899  -0.0178342    0.0058761
C     4.9222110    1.1190379    0.0089773
C     3.5453838    1.0191100    0.0073493
H     2.9341861    1.9090374    0.0071708
C     5.5891062    2.4641597    0.0152150
F     6.3838413    2.6264995    1.1043532
F     4.7042067    3.4895761    0.0195881
F     6.3844059    2.6364199  -1.0719253
H     6.8000543    0.0708754    0.0081819
C     5.9205611  -2.5203034  -0.0068693
F     5.6451897  -3.2981879    1.0730359
F     5.6568406  -3.2776664  -1.1042321
F     7.2513220  -2.2909961    0.0022852
H     3.2629009  -2.3607879  -0.0050178
C    -0.0010423    2.1135618  -0.0136354
C    -0.0512860    2.9204804  -1.2325247
C    -0.2847531    4.3411985   -0.7633112
THF*L3 (Fig. S18, left entry 3):

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H  -0.9432710  2.4664471  1.8639669
N  -1.2898876  3.0593918  1.1141633
S  -2.9927913  2.9963992  1.0938517
O  -3.4057918  3.1609385  2.4953723
C  -3.4525854  3.9122503  0.0402762
C  -3.3647558  1.3168429  0.5716656
C  -3.4917917  0.3304270  1.5372994
C  -3.6443377  -0.9812867  1.1193595
C  -3.6535631  -1.3019177  -0.2352380
C  -3.5235369  -0.2922057  -1.1752221
N  -3.3875634  1.0350098  -0.7809187
H  -3.2858045  1.8229108  -1.5105531
C  -3.5436915  -0.5962419  -2.6465111
F  -3.5291345  -1.9217934  -2.9100647
F  -4.6513381  -0.0860014  -3.2456565
F  -2.4753038  -0.0535310  -3.2851636
H  -3.7522812  -2.3287892  -0.5457031
C  -3.8546610  -2.0743296  2.1301790
F  -3.2109748  -3.2190119  1.7897133
F  -4.2964282  -1.7326218  3.3642706
F  -5.1737703  -2.3938163  2.2413375
H  -3.4442242  0.5851477  2.5838476
C  -0.6086870  2.8706944  -0.1178262
C  -0.4701024  3.9572622  -0.9744693
C  -0.1817745  3.8206954  -2.1899500
C  -0.7256115  2.5954824  -2.5537128
C  -0.6038592  1.5104829  -1.7016463
C  -0.0759832  1.6277430  -0.4927200
N  -0.2872439  0.4719008  0.3100251
S  -0.7365627  0.2084458  1.6394066
O  -0.3715387  -1.1101536  2.1719635
O  -0.6694037  1.4186236  2.4827655
C  -2.3875543  0.1230738  0.9386673
C  -3.0569090  1.3060520  0.6559390
C  -4.2835468  1.2277884  0.0167244
C  -4.8326440  -0.0033730  -0.3308814
C  -4.1367153  -1.1654065  -0.0375292
C  -2.9011430  -1.1131387  0.5981261
H  -2.3465332  -2.0119550  0.8150655
C  -4.7053742  -2.5147980  -0.3776595
F  -5.8056465  -2.4409771  -1.1548586
$$\begin{array}{c|c|c|c}
F & 5.0518458 & -3.2041299 & 0.7407174 \\
F & 3.8007491 & -3.2832349 & -1.0390646 \\
H & 5.7887934 & -3.2832349 & -1.6771239 \\
C & 5.0484752 & 2.4740431 & -0.8272947 \\
F & 6.2865286 & 2.4756094 & -1.0390646 \\
F & 4.4279460 & 3.6005302 & 0.0750129 \\
H & 0.1028761 & 0.5535850 & -1.9676421 \\
H & 6.8818149 & 2.0281550 & -0.0112315 \\
O & 0.1193732 & -2.0087676 & -1.0508403 \\
C & 0.2605639 & -3.2364232 & -1.5175642 \\
N & 1.1175724 & 0.4082978 & 0.0015063 \\
C & 2.4753422 & 0.1251753 & 0.0007780 \\
F & 5.3306302 & 3.0895441 & 1.0870675 \\
F & 5.3198910 & 3.0940505 & -1.0898484 \\
F & 2.8950299 & 2.2324577 & 0.0022498 \\
N & 0.9212373 & 1.4227888 & 0.0019846 \\
C & 2.4755448 & 0.1256126 & 0.0007780 \\
F & 3.0492587 & -1.1463338 & -0.004474 \\
C & -4.4309139 & -1.2826751 & -0.0014299 \\
\end{array}$$

Cl-\#1 \textit{(Fig. 9, entry 1; Fig. S18, right entry 1)}:

$$\begin{array}{c|c|c|c}
S & -0.0001610 & -2.6018251 & -0.0022204 \\
C & -0.0001609 & -3.782175 & 0.0003833 \\
N & 1.1175724 & 0.4082978 & 0.0015063 \\
C & 2.4753422 & 0.1251753 & 0.0009105 \\
C & 3.3256694 & 1.2402611 & -0.0014877 \\
C & 4.6991491 & 1.0781246 & -0.0023962 \\
C & 5.2776980 & -0.1863569 & -0.0007923 \\
C & 4.3060973 & -1.2829071 & 0.0019888 \\
C & 3.0491016 & -1.146320 & 0.0028745 \\
H & 2.4093951 & -2.011887 & 0.0049877 \\
C & 4.9845478 & -2.6779119 & 0.0030198 \\
F & 6.3370723 & -2.712528 & 0.0072099 \\
F & 4.5714811 & -3.3863734 & 1.0892966 \\
F & 4.5783255 & -3.3849714 & -1.0868916 \\
H & 6.3478101 & -0.3076244 & 01.0018009 \\
C & 5.5579028 & 2.3096149 & -0.0042353 \\
F & 6.8818149 & 2.0281550 & -0.0112315 \\
F & 5.3306302 & 3.0895441 & 1.0870675 \\
F & 5.3198910 & 3.0940505 & -1.0898484 \\
H & 2.8950299 & 2.2324577 & 0.0022498 \\
H & 0.9212373 & 1.4227888 & 0.0019846 \\
N & 1.1175334 & 0.4086121 & 0.0014238 \\
C & -2.4755448 & 0.1256126 & 0.0007780 \\
C & -3.0492587 & -1.1463338 & -0.004474 \\
C & -4.4309139 & -1.2826751 & -0.0014299 \\
\end{array}$$
Cl–*L2 (Fig. 9, entry 2, Fig. S18, right entry 2):

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### S43

| Atom | X      | Y      | Z   |
|------|--------|--------|-----|
| F    | 5.1326033 | 3.4899792 | 1.0785142 |
| F    | 6.8938325 | 2.7307591 | 0.0468653 |
| F    | 5.1921185 | 3.4646125 | -1.0785142 |
| F    | 7.2531158 | -2.0261198 | 0.0785142 |
| F    | 5.6407356 | -3.0266190 | -1.0952900 |
| F    | 5.6653056 | -3.0213156 | 1.0815559 |
| H    | 3.263926 | -2.0906808 | 0.0094396 |
| Cl   | 0.0000139 | 2.7337886 | 0.0033980 |

**Cl-L3 (Fig. 9, entry 3, Fig. 18, right entry 3):**

| Atom | X      | Y      | Z   |
|------|--------|--------|-----|
| H    | -1.5053231 | -2.5131281 | 1.4250046 |
| N    | -1.9853172 | -1.9213031 | 2.125326 |
| S    | -3.5853357 | -1.6488181 | 1.6513204 |
| O    | -4.0658049 | -2.9316603 | 1.1128774 |
| O    | -4.2765945 | -0.9810402 | 2.7675980 |
| C    | -3.4833004 | -0.4615293 | 0.3044061 |
| C    | -3.3407342 | -0.9293366 | -0.9912813 |
| C    | -3.1375128 | -0.0059734 | -2.0047903 |
| C    | -3.0604950 | 1.3527370 | -1.7263224 |
| C    | -3.2002523 | 1.7885242 | -0.4172311 |
| C    | -3.4282528 | 0.8857673 | 0.6129393 |
| H    | -3.536505 | 1.2199869 | 1.6327113 |
| C    | -3.1421082 | 3.2531418 | -0.0945014 |
| F    | -4.3948714 | 3.7708951 | 0.0781351 |
| F    | -2.4682424 | 3.5012181 | 1.0522336 |
| F    | -2.5568869 | 3.9840572 | -1.0686253 |
| H    | -2.8591427 | 2.0545557 | -2.5169819 |
| C    | -3.0367776 | -0.4800584 | -3.4262233 |
| F    | -4.2744857 | -0.5425198 | -4.0069463 |
| H    | -2.948222 | 0.3412517 | -4.2024323 |
| F    | -2.5061335 | -1.7163848 | -3.5269835 |
| H    | -3.3521855 | -1.9882315 | -1.1944121 |
| C    | -1.2454275 | -0.8116045 | 2.6215359 |
| C    | -1.3797984 | -0.4891351 | 3.9666271 |
| C    | -0.7130680 | 0.5940890 | 4.5128768 |
| C    | 0.1208057 | 1.3519868 | 3.7034735 |
| C    | 0.2808407 | 1.0381970 | 2.3638392 |
| C    | -0.4086337 | -0.0329349 | 1.7941152 |
| N    | -0.3418372 | -0.3545430 | 0.4296172 |
| S    | 0.4796545 | 0.5044853 | -0.7367186 |
| O    | 0.2173463 | 1.9428671 | -0.5740482 |
| O    | 0.1735376 | -0.1828255 | -1.9995114 |
| C    | 2.2317546 | 0.2173885 | -0.4023795 |
| C    | 2.6760091 | -1.0933703 | -0.3373181 |
| C    | 4.0288287 | -1.3213984 | -0.1303855 |
| C    | 4.9181347 | -0.2619645 | 0.0118676 |
| C    | 4.4381168 | 1.0386946 | -0.0473193 |
| C    | 3.0866002 | 1.2926458 | -0.2570480 |
| H    | 2.7065578 | 2.3019379 | -0.2936357 |
| C    | 5.3784760 | 2.2044243 | 0.0665194 |
| F    | 4.8856131 | 3.1794180 | 0.8704451 |
Cp₂TiCl₂*L₁ (Fig. 13, entry 1):

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S   2.1127157  2.8310114  -2.4729179
C   0.9894533  2.1396831  -1.4320561
N   1.2648653  1.1161134  -0.5822061
C   2.5479210  0.6366144  -0.2913847
C   3.5514224  1.5056670   0.1361456
C   4.7968403  0.9974160   0.4546324
C   5.0672094  -0.3676678   0.3694500
C   4.0571152  -1.2171182  -0.0440616
C   2.7992079  -0.7229942   0.3768991
H   2.0142075  -1.3835898   0.7070892
C   4.2855849  -2.6966439  -0.1228033
F   3.6120959  -3.3616448   0.8587712
F   5.5856534  -3.0407727  -0.0039722
F   3.8453154  -3.2153829  -1.3005852
H   6.0439545  -0.7496258   0.6228443
C   5.9029118  1.9090578   0.8984413
F   5.500471   3.1884729   1.0663230
F   6.9239902  1.9344477  -0.0021802
F   6.4468706  1.5097248   2.0792827
C   3.3416346  2.5582335   0.2181400
H   0.5070425  0.4698564  -0.3792626
N  -0.3020441  2.5708228  -1.4479139
C  -1.3200316  2.4616654  -0.5047304
C  -1.1032151  2.1740480   0.8448364
C  -2.1730181  2.1756890   1.7254992
C  -3.4626028  2.4741827  -1.3071445
C  -3.6648531  2.7671458  -0.0357000
C  -2.6176714  2.7490532  -0.9406149
H  -2.7877786  2.9519304  -1.9864294
C  -5.0623854  3.0419490  -0.5110323
F  -5.0962588  3.6865835  -1.7009652
F  -5.7617835  3.8019933   0.3679932
F  -5.7732148  1.8903320  -0.6734879
H  -4.2826515  2.4787704   2.0066889
C  -1.9644013  1.8304290   3.1724498
F  -0.6624006  1.6772420   3.4999357
F  -2.5934395  0.6702343   3.5044067
F  -2.4678290  2.7863032  3.9982436
H  -0.1133258  1.9617539  1.2080572
H  -0.5464751  3.0688620  -2.2946030
Cl  -0.4408885  -1.3994570  0.8264040
Ti  -1.5947706  -2.3408309  -1.0475762
Cl  -0.8807259  -0.6733750  -2.5571791
C    0.3322714  -3.4289236  -2.0140920
C    0.2040188  -3.9122188  -0.7058553
C    -1.0341645  -4.5821929  -0.6012397
C    -1.6441406  -4.5593337  -1.8783217
C    -0.8175616  -3.8221738  -2.7409740
H    -1.0358232  -3.5655367  -3.7634793
H    -2.5944016  -4.9902918  -2.1310120
H    -1.4398491  -5.0275613  0.2908038
H     0.8946867  -3.7474254  0.0998118
H     1.1349778  -2.8245327  -2.3949269
C    -3.7193908  -3.1735902  -0.4063472
C    -3.3919412  -2.1599245  0.5047380
C    -3.3369531  -0.9367772  -0.2039370
C    -3.6461234  -1.1951777  -1.5467362
C    -3.8483847  -2.5820674  -1.6900762
C    -4.0625752  -3.1008623  -2.6080125
C    -3.6580314  -0.4713922  -2.3404197
C    -3.0563456  0.0133339  0.2079883
C    -3.1659017  -2.2946479  1.5476773
C    -3.8145364  -4.2196535  -0.1805278

\textit{Cp}_2TiCl_2*L_2 (Fig. 13, entry 2):

H     0.9846716  0.2699952  1.0525515
N    1.3777490  1.1570117  0.7479862
C    0.5052928  2.0521635  0.2734369
C   -0.9006621  1.9778504  0.2003064
N   -1.7158229  0.9804437  0.5699942
C   -3.1091467  0.9184031  0.5747977
C   -3.9229865  1.9462622  0.1123816
C   -5.3020957  1.7933259  0.1569318
C   -5.8934358  0.6370018  0.6408444
C   -5.0649075  -0.3854648  1.0910328
C   -3.6887856  -0.2522209  1.0708629
H   -3.0555601  -1.0500118  1.4285084
C   -5.6846562  -1.6251752  1.6696620
F   -4.8552963  -2.6970432  1.6149998
F   -6.8244350  -1.9767657  1.0290529
F   -6.0119062  -1.4556474  2.9804179
H   -6.9647012  0.5276864  0.6667642
C   -6.1470069  2.9223199  -0.3641864
F   -6.0027975  3.0742039  -1.7085442
F   -5.7998422  4.1093787  0.1959209
F   -7.4652730  2.7462243  -0.1290020
H   -3.4851225  2.8542167  -0.2774990
H   -1.2615915  0.1295633  0.8976634
C   -0.9972292  3.3272639  -0.395189
O   -1.8747737  4.0687721  -0.8026153
Cp2TiCl2*2L2 (vdW complex, Fig. S19):

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H -0.7043895  2.6431705  -0.1764888
N -1.2083385  1.9957523   0.4108054
C -0.4677528  1.1069833  1.0871276
C  0.9314157  0.9072406  1.0731071
N  1.8778100  1.5557850  0.3899341
C  3.2534660  1.3132327  0.3294516
C  3.8739806  0.2784075  1.0173179
C  5.2486424  0.1138292  0.9045800
C  6.0188474  0.9501155  0.1142789
C  5.3796289 -0.5706175
C  4.0138779 -0.4719901
H  3.5287978 -1.0042712
C  6.2192287 -1.4192970
F  7.1536598 -0.6803032
F  5.4953566 -2.0610804
F  6.9005648 -0.2683032
H  3.2949521 -0.3873345
H  1.5612511 -0.2469117
C  0.8291764 -0.2009367
O  1.5801091 -0.9695022
C -0.6688390  0.0652848
O -1.6050519 -0.5459056
C -2.5955524  2.1607341
C -3.4775549  1.3134954
C -4.8404464  1.5346001
C -5.3530546  2.5795073
C -4.4595355  3.4135946
C -3.9090671  3.2176878
H -2.4049872  3.8701257
C -4.9912054  4.5870055
F -5.2330243  5.6506670
F -6.1605219  4.3074723
F -6.5070252 -0.1325741
H -6.4171036  2.7326548
C -5.8098632  0.6077710
F -6.7315955  1.2844692
F -6.5070252 -0.1325741
F -5.2078286 -0.2665922
H -3.1022426  0.5003489
Cl -0.1735984 -4.4264176
Ti -0.7729249 -3.2809083
Cl  0.8301289 -1.5486320
C -0.4471718 -3.6101181
C -1.2612787 -4.6718113
C -0.5070708 -5.4361573
C  0.7916109 -4.8734690
C  0.8286385 -3.7642416

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Cp₂TiCl₂*L₃ (Fig. 13, entry 3):

77
|     | X-coord  | Y-coord  | Z-coord  |  
|-----|----------|----------|----------|
| C   | -2.3142873 | -3.5605321 | 0.5458138  |
| C   | -1.1692795  | -3.5240528 | -0.2440266 |
| H   | -1.1235969  | -4.0673944 | -1.1727351 |
| C   | -3.4720945  | -4.4083150 | 0.0947970  |
| F   | -3.7177236  | -2.6980088 | -1.2303623 |
| F   | -3.2238065  | -5.7300758 | 0.3063501  |
| F   | -4.6183390  | -4.1167333 | 0.7461171  |
| H   | -3.2657259  | -2.8836826 | 2.3458838  |
| C   | -1.3488400  | -1.3711913 | 3.4547213  |
| F   | -1.8288621  | -2.1274753 | 4.4733553  |
| F   | -0.1542924  | -0.8827206 | 3.8520898  |
| F   | -2.1904063  | -0.3110123 | 3.3294547  |
| H   | 0.7545102   | -1.5443846 | 1.7234291  |
| H   | 1.5950768   | -0.4564146 | -1.3899090 |
| H   | -0.3902758  | -2.9984531 | -3.1566982 |
| H   | -2.4690168  | -2.4736275 | -4.3394862 |
| H   | -3.2925011  | -0.1325034 | -4.449637  |
| H   | -2.0173385  | 1.6527732  | -3.2853636 |
| Cl  | 6.4578602   | 2.7309178  | -0.1852728 |
| Ti  | 5.2994516   | 0.7177306  | 0.3074482  |
| Cl  | 3.6246334   | 1.1076201  | -1.3270105 |
| C   | 6.5781067   | -0.2363868 | -1.4733170 |
| C   | 7.4461582   | -0.1094852 | -0.3693921 |
| C   | 6.9684224   | -0.9335022 | 0.6629781  |
| C   | 5.8061230   | -1.5937518 | 0.1876830  |
| C   | 5.5804193   | -1.1713327 | -1.1320906 |
| H   | 4.7480532   | -1.4607075 | -1.7459188 |
| H   | 5.2018078   | -2.2962326 | 0.7304201  |
| H   | 7.4087065   | -1.0457986 | 1.6365357  |
| H   | 8.2911118   | 0.5518245  | -0.305536  |
| H   | 6.6326585   | 0.3260105  | -2.3887330 |
| C   | 3.9321370   | 2.0510587  | 1.7465136  |
| C   | 3.3217976   | 0.7848309  | 1.6500831  |
| C   | 4.1908366   | -0.1670021 | 2.2048387  |
| C   | 5.3437869   | 0.5166155  | 2.6705387  |
| C   | 5.1706437   | 1.8845202  | 2.3982123  |
| H   | 5.8880203   | 2.6604561  | 2.5940266  |
| H   | 6.1938263   | 0.0704041  | 3.1536278  |
| H   | 4.0056930   | -1.2232163 | 2.2646859  |
| H   | 2.3789033   | 0.5802582  | 1.1802754  |
| H   | 3.5440059   | 2.9680097  | 1.3399264  |
Cp2TiCl2–*L1 (Fig. 10, entry 1):

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|   |   |   |   |
|---|---|---|---|
|   | -0.0848429 | 3.4536451 | -0.2407508 |
| C | -0.0200604 | 1.7864968 | -0.0595212 |
| N | -1.1077455 | 0.9591329 | -0.1148383 |
| C | -2.4611715 | 1.2510316 | -0.0625363 |
| C | -2.9943678 | 2.3598030 | 0.5934303 |
| C | -4.3709682 | 2.5376528 | 0.6287069 |
| C | -5.2394295 | 1.6307170 | 0.0399857 |
| C | -4.6970359 | 0.5142692 | -0.5872532 |
| C | -3.3289573 | 0.3223793 | -0.6472546 |
| H | -2.9102332 | -0.5372403 | 1.1490325 |
| C | -5.6362026 | -0.4897024 | -1.1850378 |
| F | -5.0016917 | -1.4730534 | -1.8637793 |
| F | -6.5121198 | 0.0839391 | -2.0531835 |
| F | -6.3938109 | -1.1001284 | 0.2307725 |
| H | -6.3062101 | 1.7802157 | 0.0770021 |
| C | -4.9245945 | 3.7766044 | 1.2695901 |
| C | -6.1782503 | 3.6015169 | 1.7540971 |
| F | -4.1636232 | 4.2139146 | 2.3030322 |
| F | -4.9973359 | 4.8093898 | 0.3810650 |
| H | -2.3404151 | 3.0656883 | 1.0733431 |
| H | -0.8956464 | 0.0013467 | 0.4224363 |
| N | 1.1041768 | 1.0446352 | 0.1481148 |
| C | 2.4552736 | 1.3344352 | 0.0362897 |
| C | 2.9877071 | 2.5093134 | -0.4929654 |
| C | 4.3660152 | 2.6633997 | -0.5712588 |
| C | 5.2395298 | 1.6797003 | -0.1364495 |
| C | 4.6976926 | 0.5085298 | 0.3831232 |
| C | 3.3110665 | 0.3289202 | 0.4693034 |
| H | 2.9163231 | -0.5802899 | 0.8793732 |
| C | 5.6311384 | -0.5862454 | 0.8078011 |
| F | 6.1662606 | -1.2328543 | -0.2664328 |
| F | 6.6808928 | -0.1148352 | 1.5288876 |
| F | 5.0292733 | -1.5305776 | 1.5666560 |
| H | 6.3065907 | 1.8151275 | -0.1992742 |
| C | 4.9183494 | 3.9656515 | -1.0725479 |
| F | 4.1139639 | 4.5558044 | -1.9896627 |
| F | 6.1371893 | 3.8305000 | -1.6495507 |
| F | 5.0711783 | 4.8657549 | -0.053310 |
| H | 2.3261858 | 3.2884706 | -0.8268471 |
| H | 0.9209361 | 0.0980819 | 0.5043260 |
| Cl | -0.3724426 | -1.6995490 | -1.6357736 |
| Ti | 0.0174420 | -3.5332663 | 0.0784486 |
| Cl | 0.5527645 | -1.6607019 | 1.7162789 |
| C | -2.3661705 | -3.7107943 | -0.3102950 |
| C | -1.8381584 | -5.0099200 | -0.3343671 |
| C | -1.3143180 | -5.2885728 | 0.9519528 |
| C | -1.4972927 | -4.1517924 | 1.7583591 |
| C | -2.1435958 | -3.1677929 | 0.9688922 |
| H | -2.3714930 | -2.1641225 | 1.2792916 |
| H | -1.1716846 | -4.0324868 | 2.7767476 |
| H | -0.8340045 | -6.2031351 | 1.2521738 |
| H | -1.8172109 | -5.6677643 | -1.1868751 |
\begin{verbatim}
Cp2TiCl2-*L2 (Fig. 10, entry 2):
\end{verbatim}
\[
\begin{align*}
\text{Cp}_2\text{TiCl}_2\text{*L}_3 \ (\text{Fig. 10, entry 3}): \\
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\end{align*}
\]
Cp₂TiCl₂-L₃ (Fig. 10, entry 4):

|   | 3.4680526 | 2.4219320 | 0.0926981 |
|---|---|---|---|
| H | 3.6046854 | 2.3827726 | -0.9148040 |
| C | 2.3829019 | 2.3082545 | -1.6387991 |
| C | 2.303109 | 2.9282089 | -2.8795640 |
| C | 1.1259874 | 2.883033 | -3.6110162 |
| C | 0.0083473 | 2.2494836 | -3.0907541 |
| C | 0.0712973 | 1.6368437 | -1.8492141 |
| C | 1.2579507 | 1.6449548 | -1.1242270 |
| N | 1.3534942 | 0.8935176 | 0.0755871 |
| S | 1.2626571 | 1.6383076 | 1.5746147 |
| O | 2.1263548 | 2.8409167 | 1.5023799 |
| O | 1.5215685 | 0.5923521 | 2.5731143 |
| C | -0.4197135 | 2.2201419 | 1.8000715 |
| H | -0.1744063 | 3.8662168 | 0.4440453 |
| C | 2.6215383 | 4.9699276 | 0.5156626 |
| F | 2.0542224 | 6.1071251 | 1.0085448 |
| F | 3.9614403 | 5.1484093 | 0.5758289 |
| H | -0.4034721 | 3.4145362 | 2.2516612 |
| C | -0.3015053 | 3.0850518 | 2.1241460 |
| C | -0.1603675 | 3.7537208 | 1.2647942 |
| C | -0.8445886 | 3.334892 | 1.1011198 |
| H | -0.1744063 | 3.8662168 | 0.4440453 |
| C | -0.6215383 | 4.9699276 | 0.5156626 |
| F | -0.2054224 | 6.1071251 | 1.0085448 |
| F | -3.9614403 | 5.1484093 | 0.5758289 |
| H | -3.2883199 | 4.9153162 | -0.7978579 |
| C | -4.0345721 | 3.4145362 | 2.2516612 |
| C | -3.4936200 | 1.2676980 | 3.7519843 |
| F | -3.6946323 | 2.0064999 | 4.8837131 |
| F | -3.0360598 | 0.0634052 | 4.1560021 |
| F | -4.7183586 | 1.0628788 | 3.2110402 |
| H | -0.8995951 | 0.6329706 | 3.1503373 |
| H | 0.7736056 | 0.0303418 | 0.0643885 |
| H | -0.7955805 | 1.1459649 | -1.4262265 |
| H | -0.9185862 | 2.2334100 | -3.6476943 |
| H | 1.0786405 | 3.373965 | -4.5765396 |
| H | 3.1708126 | 3.435494 | -3.259273 |
| S | 4.8324148 | 1.2707820 | -1.2797046 |
| O | 5.0787787 | 1.3468397 | -2.7284875 |
| O | 5.9009033 | 1.5528792 | -0.3053625 |
| C | 4.1635464 | -0.3614460 | -0.9266080 |
| C | 4.1178192 | -0.7901715 | 0.3923158 |
| C | 3.5575085 | -2.0254881 | 0.6632823 |
| C | 3.0387646 | -2.8136345 | -0.3605480 |
| C | 3.108191 | -2.3596985 | -1.6663610 |
| C | 3.6639493 | -1.1227746 | -1.9648657 |
| H | 3.7091245 | -0.7597074 | -2.9796474 |
| C | 2.6074608 | -3.2145368 | -2.7969584 |
| F | 3.6542881 | -3.7615781 | -3.4883164 |
| F | 1.8876852 | -2.5082624 | -3.7000441 |
| F | 1.8398224 | -4.2450528 | -2.3873458 |
| H | 2.5769051 | -3.7601941 | -0.1319649 |
| C | 3.4970275 | -2.5534405 | 2.0681460 |
| F | 4.1920739 | -3.7262328 | 2.1803794 |
| F | 4.0317632 | -1.7037874 | 2.9727124 |
\begin{verbatim}
F    2.2343046  -2.8220077  2.4632591
H    4.4984459  -0.1651766  1.1841144
Cl  -0.2212261  -1.7749504  -0.2389331
Ti  -2.6229695  -1.9478896  -1.0224365
Cl  -2.9256711   0.4215734  -0.2924766
C   -3.0990191  -2.4564615  -0.2924766
C   -2.5417345  -3.6338321   0.6722055
C   -3.5404652  -1.7749504  -0.2389331
C   -4.5404652  -2.2296040  -0.3562112
H   -4.9895187  -1.3851623   0.7595090
H   -5.3739936  -3.3239988  -1.0338560
H   -3.2582897  -4.9733171  -0.9340336
H   -1.5732400  -4.0375115   0.9064563
C   -2.6890306  -0.7476900  -3.1468639
C   -1.4866004  -2.8446506  -3.033259
C   -3.1994674  -2.9911901   0.6390848
C   -2.6147816  -1.3315815   0.3860022
C   -3.9411117  -1.9289773  -0.4969583
C   -4.3841627  -1.6652893  -3.100142
C   -3.4841627  -1.4207319  -3.0874456
C   -2.1469106  -0.6552893  -3.0376698
H   -1.4429780  -0.1253138  -1.9267948
C   -3.9721680  -1.1385513  -2.1515476
F   -5.1588650  -0.8282480  -2.7923738
F   -5.6524520  -1.4080784  -2.9587973
F   -5.8523742  -2.9149815  -1.3094329
H   -2.2651927  -2.6946725  -1.1686769
H    0.3021896   0.9689200   0.5322676
N    1.3939819   3.1868187   0.5664179
C    2.3648958   2.3961189   0.5664179
C    3.6194369   2.8939429  -0.5280125
C    4.6150173   1.5589298  -0.1030883
C    4.3827579   0.9291187  -1.3170286
\end{verbatim}

\textit{Cp2TiCl*L1 (Fig. S20, left entry 1):}

S  -0.9677908  4.2553882  1.0781022
C   0.0514407  2.9911901  0.6390848
N  -0.3718861  1.7219163   0.3959220
C   -1.7199819  1.3315815  -0.3860022
C   -2.6147816  1.9289773  -0.4969583
C   -3.9411117  1.5324805  -0.4904931
C   -4.3905765   0.5411693   0.3758476
C   -3.4841627  -0.0535649  1.2388829
C   -2.1469106   0.3295991  1.2475996
H   -1.4429780  -0.1253138  1.9267948
C   -3.9721680  -1.1385513  2.1515476
F   -5.1588650  -0.8282480  2.7923738
F   -5.6524520  -1.4080784  2.9587973
F   -5.8523742  -2.9149815  1.3094329
H   -2.2651927  -2.6946725  1.1686769
H    0.3021896   0.9689200  0.5322676
N    1.3939819   3.1868187   0.5664179
C    2.3648958   2.3961189   0.5664179
C    3.6194369   2.8939429  -0.5280125
C    4.6150173   1.5589298  -0.1030883
C    4.3827579   0.9291187  -1.3170286
| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| C    | 3.1302119 | 1.0583349 | -1.9041460 |
| C    | 2.1221334 | 1.7873876 | -1.2963916 |
| H    | 1.1590649 | 1.8936382 | -1.7676986 |
| C    | 2.9155989 | 0.4307414 | -3.2502008 |
| F    | 3.6661906 | 1.0362201 | -4.2116450 |
| F    | 3.2716153 | -0.8809665 | -3.2617538 |
| F    | 1.6303511 | 0.4921676 | -3.6543636 |
| H    | 5.1602822 | 0.3603198 | -1.8013430 |
| C    | 5.9436179 | 1.3733541 | 0.5700441 |
| F    | 6.2267651 | 2.3627424 | 1.4507118 |
| H    | 3.7964069 | 2.7710856 | 1.4769646 |
| C    | 5.9881942 | 0.2056771 | 1.2707837 |
| F    | 1.4866000 | -0.9115810 | 0.9664711 |
| Ti   | 0.1759389 | -2.8377277 | 0.4780503 |
| C    | 0.1923473 | -1.7355439 | -1.5429839 |
| C    | 0.6108949 | -2.8619113 | -1.8290824 |
| C    | -0.1488501 | -4.0129419 | -1.5491551 |
| C    | -1.4203279 | -3.5998658 | -1.0915883 |
| C    | -1.4484878 | -2.1919320 | -1.0815812 |
| H    | -2.2819596 | -1.5785771 | -0.7877234 |
| H    | -2.2169311 | -4.2457179 | -0.7658882 |
| H    | 0.1934111 | -5.0308317 | -1.6275115 |
| H    | 1.6342644 | -2.8438086 | -2.1629928 |
| H    | 0.1123721 | -0.7092628 | -1.6309069 |
| C    | -0.3695845 | -4.9166895 | 1.3765115 |
| C    | 1.0277356 | -4.7435628 | 1.5150691 |
| C    | 1.2347381 | -3.6802803 | 2.4205470 |
| C    | -0.0221018 | -3.1832304 | 2.8158716 |
| C    | -1.0186792 | -3.9396914 | 2.1649587 |
| H    | -2.0817035 | -3.7994668 | 2.2497923 |
| H    | -0.1880572 | -2.3303034 | 3.4526606 |
| H    | 2.1885580 | -3.2693157 | 2.7024108 |
| H    | 1.7920464 | -5.3245045 | 1.0264709 |
| H    | -0.8554255 | -5.6463466 | 0.7544173 |
**Cp2TiCl*L2 (Fig. S20, left entry 2):**

|  | X     | Y     | Z     |
|---|-------|-------|-------|
| H | -0.6360639 | 0.8592568 | 0.5546046 |
| N | -1.6258234 | 1.0862617 | 0.5912574 |
| C | -1.9616476 | 2.2198128 | 1.2285586 |
| C | -1.1938016 | 3.3358929 | 1.6128480 |
| N | 0.0568487  | 3.7691408 | 1.4432324 |
| C | 0.9629391  | 3.3332499 | 0.4698066 |
| C | 0.5160383  | 2.8566904 | -0.7560325 |
| C | 1.4349980  | 2.3721645 | -1.6782018 |
| C | 2.7927069  | 2.3946933 | -1.4156798 |
| C | 3.2262223  | 2.9221905 | -0.2012434 |
| C | 2.3308256  | 3.3902987 | 0.7419140 |
| H | 2.6688779  | 3.7712162 | 1.6925645 |
| C | 4.6990361  | 2.9046966 | 0.0896053 |
| C | 5.1631512  | 3.6347011 | 0.2503955 |
| H | 5.4235918  | 3.4483407 | -0.9238001 |
| F | 5.0270308  | 3.5816018 | 1.2125716 |
| H | 3.5013361  | 2.0065365 | -2.1282803 |
| C | 0.9108110  | 1.8461634 | -2.9824102 |
| F | 1.8551803  | 2.1447474 | -3.7146214 |
| F | 0.1023387  | 0.9582957 | -2.7979733 |
| F | 0.4076768  | 2.8418249 | -3.7620362 |
| H | 0.3679233  | 4.4966249 | -0.9914505 |
| C | -2.3023893 | 3.9124532 | 2.3915958 |
| O | -2.4354511 | 4.8795102 | 3.1163828 |
| C | -3.1578654 | 2.7241401 | 1.9487434 |
| O | -4.2998770 | 2.3511475 | 2.1336389 |
| C | -2.4713912 | 0.1105211 | 0.0658068 |
| C | -3.8157250 | 0.352296  | -0.2063874 |
| C | -4.5913255 | -0.6617340 | -1.2234146 |
| C | -4.0579590 | -1.9069834 | -1.0560867 |
| C | -2.7122713 | -2.1247376 | -0.7940160 |
| C | -1.9204547 | -1.1341061 | -0.2370032 |
| H | -0.8759702 | -1.3168096 | -0.0255906 |
| C | -2.0725602 | -3.4424821 | -1.1185528 |
| F | -1.1099005 | -3.3108388 | -2.0719431 |
| F | -2.9500368 | -4.3615480 | -1.5721407 |
| F | -1.4585578 | -3.9854880 | -0.0313026 |
| H | -4.6707919 | -2.6810610 | -1.4861327 |
| C | -6.0448698 | -0.3741688 | -1.0036512 |
| F | -6.7205271 | -0.1620014 | 0.1568066 |
| F | -6.2149311 | 0.7444846 | -1.7572187 |
| F | -6.6780704 | -1.3795383 | -1.6473160 |
| H | -4.2547508 | 1.3056161 | 0.0262592 |
| Cl| 1.4206714  | -0.0468921 | 1.0857970 |
| Ti| 2.3513909  | -2.2351214 | 1.0098817 |
| C | 1.0324770  | -2.6652498 | 2.9258240 |
| C | 2.2493192  | -2.1013507 | 3.3596883 |
| C | 3.2970286  | -2.9784541 | 3.0066230 |
| C | 2.7145731  | -4.0986337 | 2.3678057 |
| C | 1.3156475  | -3.8959316 | 2.3007055 |
| H | 0.6006536  | -4.5643297 | 1.8518463 |
Cp2TiCl*L3 (Fig. 11, entry 3; Fig. S20, left entry 3):

|  |   |   |   |
|---|---|---|---|
| Cl | -0.6322794 | 3.1022554 | -1.6717001 |
| Ti | -1.9454231 | 3.3143832 | 0.4398989 |
| O | -1.3265649 | 1.1914151 | 0.8846958 |
| S | -0.9902380 | -0.1637246 | 0.3704474 |
| O | -0.1638924 | -1.0372810 | 1.2140923 |
| N | 0.5653192 | -0.4144394 | -2.3647932 |
| C | 2.3503247 | -2.7205188 | -2.8054487 |
| C | 2.7097632 | -1.3904492 | -2.6679731 |
| C | 1.8359583 | -0.4696438 | -2.0925929 |
| N | 2.2178076 | 0.8956260 | -1.9817186 |
| S | 2.8084657 | 1.4441421 | -0.4740690 |
| O | 1.7236049 | 1.3505041 | 0.5090565 |
| O | 3.4813005 | 2.7205188 | -0.7548975 |
| C | 4.0311756 | 0.2180701 | 0.0188594 |
| C | 3.5834659 | -0.9220473 | 0.6649589 |
| C | 4.5096708 | -1.8967375 | 1.0090914 |
| C | 5.8591027 | -1.7267163 | 0.7259908 |
| C | 6.2765615 | -0.5686894 | 0.0827264 |
| C | 5.3649841 | -0.4129966 | -0.2881226 |
| H | 5.6862708 | 1.3131245 | -0.7881979 |
| C | 7.7309987 | -0.332532 | -0.2167698 |
| F | 8.1955797 | 0.7834616 | 0.4259047 |
| F | 7.9418975 | -0.1246440 | -1.5429732 |
| F | 8.5176428 | -1.3677907 | 0.1494689 |
| H | 6.5730021 | -2.4834223 | 1.0073823 |
| C | 4.0196758 | -3.1323257 | 1.7055776 |
| F | 3.4118382 | -2.8288615 | 2.8869764 |
| F | 3.0822559 | -3.7824358 | 0.9585774 |
| F | 4.9934428 | -4.0177897 | 1.9763995 |
| H | 2.5350051 | -1.0351237 | 0.9005435 |
| H | 2.9103365 | 1.1587610 | -2.6738893 |
| H | 3.6847244 | -1.0468222 | -2.9833869 |
| H | 3.8432196 | -3.4232061 | -3.2466763 |
| H | 0.8098279 | -4.1798622 | -2.4645968 |
Cp2TiCl(THF)*L1 (Fig. 11, entry 1; Fig. S20, right entry 1):

75

S 0.4686580  -3.2690116  -0.7444134
C 0.3317961  -2.0178369  0.3553673
N -0.8510845  -1.5536845  0.8649127
C -2.1560183  -1.8959400  0.5084663
C -2.5774876  -3.2083482  0.304431
C -3.9082846  -3.4520041  -0.0013024
C -4.8359573  -2.4213858  -0.1011763
C -4.4056343  -1.1226603  0.1253695
C -3.0792843  -0.8561398  0.4298738
H -2.7454675  0.1581786  0.5979488
C -5.3791957  0.0176771  0.9917446
F -4.8524271  1.1208935  -0.5047154
Cp₂TiCl(THF)*L₂ (Fig. 11, entry 2; Fig. S20, right entry 2):

| Atom | X    | Y    | Z    |
|------|------|------|------|
| H    | -1.1716508 | -0.4619317 | -0.8261890 |
| N    | -1.6252775 | -1.3141005 | -0.4873437 |
| C    | -0.8111256 | -2.2839875 | -0.0505192 |
| C    | 0.6008528 | -2.3338644 | -0.0333118 |
| N    | 1.4895862 | -1.4194950 | -0.4429288 |
| C    | 2.8821810 | -2.5790277 | -0.0140924 |
| C    | 3.6076489 | -2.5179523 | -0.0933910 |
| C    | 4.9923054 | -2.5179523 | -0.0933910 |
| N    | 5.6801869 | -1.4838772 | -0.6303827 |
| C    | 4.9422043 | -0.3984104 | -1.0868668 |
| C    | 3.5592782 | -0.3998995 | -1.0172750 |
| C    | 2.9994825 | -0.4605165 | -1.3775216 |
| C    | 5.6437565 | -1.3764380 | -1.7346102 |
| F    | 5.0605967 | -0.9492125 | -1.4356256 |
| F    | 5.6286620 | -0.5656662 | -3.0923620 |
| F    | 6.9410220 | -0.8567900 | -1.3669059 |
| H    | 6.7559160 | -1.4845094 | -0.6862907 |
| C    | 5.7336776 | -3.7614101 | 0.4280128 |
| F    | 5.3804658 | -4.8949965 | -0.2332412 |
| F    | 5.4649681 | -3.9834255 | 1.7418117 |
| F    | 7.0746887 | -3.6429377 | 0.3162788 |
| H    | 3.0959068 | -3.4332314 | 0.4063350 |
| H    | 1.1006696 | -0.5382967 | -0.7709631 |
| C    | 0.5978696 | -3.6881784 | 0.5661625 |
| O    | 1.4177862 | -4.5128473 | 0.9283521 |
| C    | -0.9116776 | -3.6377201 | 0.5438229 |
| O    | -1.7989329 | -4.4048151 | 0.8835180 |
| C    | -3.0193196 | -1.2911607 | -0.5502498 |
| C    | -3.6096872 | -0.1970695 | -1.1887172 |
| C    | -4.9864914 | -0.1152133 | -1.2837400 |
| C    | -5.8060666 | -1.1075659 | -0.7543291 |
| C    | -5.2950999 | -2.1872679 | -0.1291152 |
| C    | -3.8248468 | -2.2895820 | -0.0154581 |
| H    | -3.3809181 | -3.1449204 | 0.4731619 |
| C    | -6.0352693 | -3.3007837 | 0.4469797 |
| F    | -7.3636007 | -3.0869208 | 0.3224448 |
| F    | -5.7683899 | -4.4872667 | -0.1613914 |
| F    | -5.7850021 | -3.4817375 | 1.7693066 |
| H    | -6.8778593 | -1.0359395 | -0.8373752 |
| C    | -5.6318395 | 1.0806664 | -1.9233230 |
| F    | -6.6812511 | 0.7347673 | -2.7086003 |
| F    | -6.1177221 | 1.9432267 | -0.9881359 |
| F    | -4.7767968 | 1.7881428 | -2.6973214 |
Cp2TiCl(THF)*L3 (Fig. S20, right entry 3):
F  4.9101128  1.3662083  -3.0307386
H  6.5570454  -0.2968379  -2.0559737
C  7.2493354  -2.5921800  -0.7440248
F  6.7798983  -3.8583254  -0.8882661
F  7.9036692  -2.821721  -1.8832491
H  5.4748389  -2.7860219  1.2657925
C  1.2610673  -2.1318553  0.6992765
C  2.0169097  -3.1649048  0.1490623
C  1.5537604  -3.8633017  -0.9555724
C  0.3357434  -3.5448576  -1.5385186
C  -0.4249067  -2.5239284  -0.9924320
C  0.0106694  -1.8311975  0.1290808
N  -0.8514926  -0.8624486  0.7047153
S  -2.0061348  -1.3574522  1.8279600
O  -1.6148899  -0.8624486  0.7047153
O  -2.3237417  -0.1644752  2.6329209
C  -3.4335454  -1.6975137  0.7804368
C  -4.3130772  -0.6679540  0.4977906
C  -5.3812071  -0.9159154  -0.3529135
C  -5.570290  -2.1751158  -0.9108084
C  -4.6702325  -3.1895169  -0.6045066
C  -3.6002402  -2.9646432  0.2528567
H  -2.903136  -3.7530088  0.4924495
C  -4.8321283  -4.5668355  -1.1872232
F  -3.7144475  -4.9610010  -1.8501316
F  -5.8593513  -4.6497673  -2.059150
F  -5.0567735  -5.4935139  -0.220256
H  -6.3952331  -2.3586148  1.5750585
C  -6.3553719  -0.1954428  -0.6262688
F  -7.1796794  -0.0684784  -1.6593923
F  -7.638392  0.4449409  0.4565267
F  -5.7163416  1.3606961  -0.9130388
H  -4.1615669  0.3050386  0.9412941
H  -0.4729740  0.0643481  0.9305069
H  -1.3771956  -2.2490446  -1.4215454
H  -0.0178354  -4.0816229  -2.4073209
H  2.1628309  -4.6586039  -1.3621143
H  2.9610173  -3.4426512  0.5862428
Cl  0.8452009  1.7837389  1.1534845
Ti  -0.4054170  3.3924326  -0.3756155
O  -2.0257478  3.2015802  1.1218282
C  -3.3213604  3.8189612  0.8675951
C  -3.8692358  4.2090902  2.2236734
H  -3.5522929  5.2177608  2.4864912
C  -3.2170714  3.1900952  3.1484199
H  -3.7349503  2.2334410  3.099625
H  -3.1878415  3.5113491  4.1865680
C  -1.8331643  3.0638967  2.5622456
H  -1.1748929  3.8632668  2.8987483
H  -1.3580235  2.1090827  2.7340195
H  -4.9557722  4.1781812  2.2440789
H  -3.9451881  3.0761347  0.3726817
H  -3.1762405  4.6591168  0.1965829
C  -0.4417702  5.5752586  0.6765959
\[
\begin{array}{cccc}
C & -0.4528775 & 5.7569645 & -0.7165877 \\
C & 0.7669727 & 5.2465249 & -1.2266761 \\
C & 1.5068555 & 4.7183676 & -0.1536276 \\
C & 0.7520613 & 4.2268112 & -0.2159600 \\
H & 0.7520613 & 4.9220909 & 1.0280463 \\
H & 1.0303665 & 4.5957695 & 2.0141026 \\
H & 2.4615278 & 4.2268112 & -0.2159600 \\
H & 1.0668012 & 5.2417919 & -2.2592736 \\
H & -1.2478793 & 6.1981750 & -1.2945709 \\
\end{array}
\]

\[(Cp^2TiCl)2*L2 (Fig. S21, entry 1):\]

88

H 
-0.4885427
0.6485654
0.1749009

N 
-0.0334429
1.4929607
0.3969129

C 
-1.3668232
1.3718161
0.4697083

C 
-2.1926086
0.2248812
0.5930582

N 
-2.0294581
-1.0743664
0.8179822

C 
-0.9013077
-1.7162624
1.3377622

C 
-0.7104472
-3.0597796
1.0145088

C 
0.3903516
-3.7278222
1.5129633

C 
1.3151740
-3.0824923
2.3317148

C 
1.0980033
-1.7564843
2.6597242

C 
-0.0128003
-1.0695064
2.1845945

H 
-0.1853638
-0.0490449
2.4826334

C 
2.0331499
-1.0263043
3.5797049

F 
3.1535172
-1.7269119
3.8595985

F 
1.4429363
-0.7325005
4.7679145

F 
2.4333543
0.1628621
3.0506084

H 
2.1789639
-3.6108596
2.6995499

C 
0.6373988
-5.1647869
1.1548679

F 
-0.3627112
-5.7056838
0.4243901

F 
0.7859484
-5.9423642
2.2587362

F 
1.7781468
-5.3108590
0.4270329

H 
-1.4251512
-3.5586466
0.3783306

H 
-2.8906292
-1.6409162
0.7457534

C 
-3.3972007
0.9940421
0.3336719

O 
-4.6026895
0.7553743
0.1410979

Ti 
-5.7521099
-0.7639630
-0.7727859

Cl 
-4.7823311
-2.4628809
0.7921223

C 
-8.0391838
-0.5638518
-1.2331167

C 
-7.8980904
-1.5418418
-0.2264873

C 
-7.4409923
-0.8844848
0.9410895

C 
-7.2857125
0.4744004
0.6494798

C 
-7.6290366
0.6816819
-0.7015985


| Atoms | X   | Y   | Z   |
|-------|-----|-----|-----|
| H     | -7.5808204 | 1.6166440 | -1.2345559 |
| H     | -6.8841150  | 1.2166297  | 1.3170082  |
| H     | -7.1949372  | -1.3641821 | 1.8730019  |
| H     | -8.0868899  | -2.5972443 | -0.3306007 |
| H     | -3.820721   | 0.7387038  | -2.2361425 |
| C     | -4.6790701  | -2.2428865 | -2.3309000 |
| C     | -3.8616920  | -1.052239  | -2.1541626 |
| C     | -4.5554979  | 0.0189235  | -2.6599863 |
| C     | -5.8034687  | -0.4239089 | -3.1238660 |
| C     | -5.8816416  | -1.8248162 | -2.9149384 |
| H     | -6.7286637  | 2.4515638  | -3.1360219 |
| H     | -6.5770330  | 0.1975783  | -3.5382416 |
| H     | -4.2115273  | 1.0394334  | -2.6493403 |
| H     | -2.8781710  | -1.0988407 | -1.7186526 |
| H     | -4.4445658  | -3.2420091 | -2.0097354 |
| C     | -2.5598920  | 2.2452615  | 0.2652924  |
| O     | -2.7765157  | 3.4284086  | 0.0915981  |
| C     | 0.7359113   | 2.6472761  | 0.5081449  |
| C     | 2.0888738   | 2.5642958  | 0.1795666  |
| C     | 2.9017225   | 3.6772940  | 0.3151729  |
| C     | 2.3945278   | 4.8891555  | 0.7689206  |
| C     | 1.0450415   | 4.9541277  | 1.0914085  |
| F     | -0.8320997  | 3.9319017  | 1.2220678  |
| F     | -2.5598920  | -2.2452615 | 0.5375230  |
| F     | -0.1972603  | 6.8842789  | 0.5130731  |
| F     | 1.3680892   | 7.1258244  | 2.0070155  |
| F     | -0.4747605  | 6.0875918  | 2.5205373  |
| H     | 3.0324446   | 5.7494814  | 0.8730444  |
| C     | 3.6116397   | 3.5352806  | -0.0328802 |
| F     | 5.0195482   | 4.7157653  | -0.0429726 |
| F     | 5.0003368   | 2.7629781  | 0.9198686  |
| F     | 4.5604820   | 2.9318165  | -1.2085682 |
| H     | 2.4915038   | 1.6288328  | -0.1838348 |
| Cl    | 1.5723911   | -0.9879861 | -1.0575625 |
| Ti    | 3.7991138   | -1.1773206 | -1.9034295 |
| C     | 5.0200880   | -0.9736482 | -3.8835756 |
| C     | 3.9230479   | -1.8305446 | -4.1356338 |
| C     | 3.3141621   | 0.2554054  | -3.6547668 |
| C     | 4.5190602   | 0.3111922  | -3.5694443 |
| H     | 5.1091525   | 1.1723926  | -3.3063299 |
| H     | 2.4330018   | 1.0566919  | -3.4221335 |
| H     | 1.7385665   | -1.4286118 | -4.0832763 |
| H     | 3.9776430   | -2.8753935 | -4.3926466 |
| H     | 6.0568909   | -1.2512245 | -3.9256181 |
| C     | 4.4900680   | -1.0919307 | 0.3555353  |
| C     | 4.2075389   | -2.4356658 | 0.0439045  |
| C     | 5.1085800   | -2.8596763 | -0.9556390 |
| C     | 5.9629655   | -1.7691656 | -1.2436434 |
| C     | 5.5676413   | -0.6690881 | -0.4467641 |
| H     | 6.0116682   | 0.3115959  | -0.4511829 |
| H     | 6.7743661   | -1.7746762 | -1.9472835 |
| H     | 5.1449293   | -3.8367276 | -1.4082472 |
| H     | 3.3939917   | -3.0129051 | 0.4453448  |
(Cp<sub>2</sub>TiCl)_{2}(THF)*L<sub>2</sub> (Fig. 12; Fig. S21, entry 2):

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H     0.6425906  0.9848294  -0.2216549
N     0.0789958  1.7945666  0.0713549
C    -1.2469791  1.6808536  -0.0282949
C    -2.1100201  0.5653777  -0.1356102
N    -2.0015488  -0.7661184  -0.0730058
C    -1.1244677  -1.5145105  0.7051831
C    -0.4231387  -0.9490103  1.7675029
C     0.3837445  -1.7524345  2.5572984
C     0.4980845  -3.1151856  2.3220185
C     0.2207712  -3.6663387  1.2674313
C    -1.0261361  -2.8834090  0.4575817
H    -1.5797168  -0.3593063  1.9890585
H    -2.7569274  -0.5560400  3.7721330
O    -4.4533533  1.2501955  -0.7400412
Ti   -5.9721022  -0.1932428  -0.6383100
Cl   -4.3953569  -1.7529010  -1.8130647
C    -5.4830928  -1.8211293  1.0968035
C    -4.9891090  -0.5747135  1.5149332
C    -6.0828816  0.3143253  1.6512567
C    -7.2504212  -0.4007343  1.3220421
C    -6.8778623  -1.7168639  0.9532543
C    -7.5416728  -2.4957678  0.6175643
C    -8.2511642  -2.0089649  1.3269274
C    -6.0288885  1.3510779  1.9391509
H    -3.9538821  -0.3318559  1.6728035
H    -4.8917001  -2.6857435  0.8543694
C    -6.4844813  0.4460853  -2.8501391
C    -7.3214516  -0.6445922  -2.5089223
C    -8.1904492  -0.2151763  -1.4927949
C    -7.8937982  1.1401238  -1.2018217
C    -6.8596905  1.5483261  -2.6558067
H    -6.3699037  2.5063230  -2.0368485
H    -8.3632441  1.7439693  -0.4438185
H    -8.9313123  -0.8185688  -0.9980097
H    -7.2678511  -1.6365818  -2.922860
H    -5.6749798  0.4221236  -3.5582663
C    -2.3758679  2.6194358  -0.3164246
O    -2.5149493  3.8203100  -0.4271522
C     0.7712014  2.9947796  0.2558150
