Supporting Information

For

Metathesis Activity Encoded in the Metallacyclobutane Carbon-13 NMR Chemical Shift Tensors

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Contents:

1. Experimental Section S2
2. Computational Details S3
3. All Calculated Compounds S4
4. Selected Structural Parameters of Metallacyclobutanes S5
5. 13C{1H} Solid-State NMR Spectra S6
6. NCS Analysis S9
7. Graphical Representations of the Results of the NCS Analysis S11
8. Graphical Representations of the Calculated Shielding Tensors S14
9. MO-Diagram of Cp2TiCH2CR2CH2 (Ti-CB) S16
10. Reactivity of Ru-CB’ and Ru-CB S17
11. Phase Relationship of Orbitals in FCl and in Metallacyclobutanes S18
12. Shielding Tensors of CH2, CH22+, and Cp2Ti(μ2-CH2)2TiCp2 S18
13. X-ray Crystallographic Analysis S19
14. Optimized Structures of all Calculated Species S20
15. References S35
1. Experimental section

General

All experiments involving air- and moisture-sensitive compounds were performed under argon by using standard Schlenk techniques or argon-filled gloveboxes. Pentane, toluene, and diethyl ether were purified using a double MBraun SPS alumina column, and were degassed using three freeze-pump-thaw cycles before use. THF, C₆H₆, and C₆D₆ were distilled from Na/Benzophenone. Solution ¹H, ¹³C and ³¹P NMR spectra were recorded on Bruker DRX 200 and DRX 300 spectrometers, and the magnetic fields were referenced by the deuterium signal of the d-solvent used. The ¹H and ¹³C spectra were additionally referenced setting the chemical shifts of the residual C₆H₆ signal in C₆D₆ at 7.16 and 128.1 ppm, respectively. The solid-state ¹H and ¹³C NMR spectra were obtained on Bruker Avance III 400, 600, and 700 MHz spectrometers using a 2.5, 3.2, or 4 mm probe, and the magnetic fields were externally referenced by setting the downfield ¹³C signal of adamantane to 38.4 ppm. The samples were loaded in a 2.5 or 4 mm zirconia rotor closed with a VESPEL drive cap, or in a 3.2 mm sapphire rotor closed with a zirconia cap with a Teflon insert placed between the sample and the cap to prevent sample spill. Cross polarization magic angle spinning (CPMAS) and spin echo type experiments were used to measure ¹³C and ¹H spectra, respectively. The ¹H excitation and decoupling radiofrequency (rf) fields were set to 71 kHz and 100 kHz for 4 mm and 2.5/3.2 mm probe, respectively. For CPMAS measurements, the CP condition was optimized to match the Hartmann-Hahn condition under MAS with minor adjustments to reach the best CP efficiency experimentally. Al(¹³CH₃)₃ (14% labeled)¹[2], 1C-¹³C-isobutene (50% labeled)³[4], Ti-Al-CB⁴[5], Ti-CB⁵[6], and Ti-ene-PMe₃⁷ were prepared according to literature procedures.

Synthesis of partially ¹³C labeled Cp₂Ti(μ-¹³CH₂)(μ-Cl)AlMe₂ (Ti-Al-CB)

To Cp₂TiCl₂ (656 mg, 2.63 mmol) dissolved in toluene (10 mL) was added a solution of Al(¹³CH₃)₃ (380 mg, 5.27 mmol, 14%¹³C-labeled) in toluene (10 mL). After stirring at room temperature for 2 days, all volatiles were removed under reduced pressure, followed by addition of AlMe₃ solution in toluene (2.0 M, 1.3 mL, 2.6 mmol). After stirring for 1 day at room temperature, all volatiles were evaporated and the resulting red residue was washed with pentane (3 mL). After drying under reduced pressure at room temperature for 10 minutes, a dark red powder of partially ¹³C labeled Cp₂Ti(μ-¹³CH₂)(μ-Cl)AlMe₂ (690 mg, 2.42 mmol, 92% yield; 10% labeled based on ¹H NMR) was obtained. ¹H NMR (C₆D₆, 200 MHz, 25 °C) δH 0.24 (s, 6H, AlMe₂), 5.61 (s, 10H, Cp), 8.30 (s, TiCH₂Al, and d, J₃-H = 126 Hz, Ti₁₃CH₂Al, 2H).

Synthesis of partially ¹³C labeled Cp₂Ti(¹³CH₃)₂CMe₂₁³CH₂ (Ti-CB)

Cp₂TiCH₂CMe₂CH₂ (960 mg, 3.87 mmol) was dissolved in CH₂Cl₂ (10 mL) at -20 °C. After cooling the reaction mixture to liquid N₂ temperature, labeled 1C-¹³C-isobutene (600 mbar, 6.7 mmol) was added. After warming the reaction mixture to 0 °C and stirring for an additional 20 minutes, all volatiles were removed under reduced pressure to give partially ¹³C labeled Cp₂Ti(¹³CH₃)₂CMe₂¹³CH₂ (960 mg, 3.87 mmol, 100% yield; 21% labeled based on ¹H NMR). The compound is thermally sensitive and was stored at -35 °C in a glovebox. ¹H NMR (C₆D₆, 200 MHz, 25 °C) δH 1.12 (s, 6H, CMe₂), 2.53 (s, CH₂CMe₂CH₂, and d, J₃-H = 138 Hz, ¹³CH₂CMe₂¹³CH₂, 4H), 5.55 (s, 10H, Cp).

Synthesis of partially ¹³C labeled Cp₂Ti(¹³CH₂)(PMe₃) (Ti-ene-PMe₃)

Partially ¹³C labeled Cp₂Ti(¹³CH₂)CMe₂(¹³CH₂) (250 mg, 1.00 mmol, 21% labeled) was dissolved in Et₂O (6 mL) at -30 °C. The dark red solution was cooled to -20 °C, and then PMe₃ (0.15 mL, 1.5 mmol) was added. The reaction mixture was stirred for 30 minutes at room temperature and occasionally evacuated to remove isobutene. The color of the reaction mixture changed to dark orange, and an orange precipitate formed. All volatiles were removed under reduced pressure to give an orange-brown residue. The residue was washed with cold pentane (3 x 3 mL), and after
drying, a yellow-brown powder of partially $^{13}$C labeled CP$_2$Ti($^{13}$CH$_2$)(PMe$_3$) was obtained (168 mg, 0.626 mmol, 63% yield; 21% labeled based on $^1$H NMR). The thermally sensitive compound was stored at −35 °C in a glovebox. $^1$H NMR (C$_6$D$_6$, 200 MHz, 25 °C) $\delta$H 0.74 (d, $^2$J$_{P-H}$ = 6.3 Hz, 9H, PMe$_3$), 5.36 (d, $^3$J$_{P-H}$ = 2.5 Hz, 10H, Cp), 12.2 (d, $^3$J$_{P-H}$ = 7.4 Hz, Ti=CH$_2$, and dd, $^1$J$_{C-H}$ = 126 Hz, $^3$J$_{P-H}$ = 7.4 Hz, Ti=$^{13}$CH$_2$, 2H). $^{31}$P $^1$H NMR (C$_6$D$_6$, 81 MHz, 25 °C) $\delta$P 11.7 (s, PMe$_3$).

**Synthesis of (PMe$_3$)$_4$Ru(CH$_2$CH$_2$CH$_2$) (Ru-CB)**

In a 100 mL Schlenk flask, (PMe$_3$)$_4$RuCl$_2$ (500 mg, 1.05 mmol) was dissolved in C$_6$H$_6$ (15 mL). To the reaction mixture was slowly added a solution of LiCH$_2$-Bu (180 mg, 2.30 mmol) in C$_6$H$_6$ (10 mL) at room temperature. The reaction mixture was stirred at room temperature for 24 h, during which a white precipitate formed. All volatiles were removed under reduced pressure to give a yellow oily residue, which was extracted with pentane (20 mL). After evaporation of the pentane solution under reduced pressure, a resulting yellow powder was dissolved in Et$_2$O (3 mL), and the resulting solution was kept at −35 °C overnight to afford yellow crystals. The supernatant was removed, and drying of the crystals under reduced pressure gave a yellow powder of Ru-CB (260 mg, 0.581 mmol, 55% yield). $^1$H NMR (C$_6$D$_6$, 200 MHz, 25 °C) $\delta$H 0.09 (t, $^3$J$_{P-H}$ = 11.9 Hz, 4H, CH$_2$CM$_2$CH$_2$), 1.01 (d, $^2$J$_{P-H}$ = 4.1 Hz, 18H, PMe$_3$), 1.31 (s, 6H, CM$_2$), 1.42 (s, 18H, PMe$_3$).

$^{13}$C($^1$H) NMR (C$_6$D$_6$, 50 MHz, 25 °C) $\delta$C -0.6 (m, $\alpha$-C), 22.4 (br, PMe$_3$), 25.6 (m, PMe$_3$), 36.6 (CM$_2$), 47.5 (β-C). $^{31}$P $^1$H NMR (C$_6$D$_6$, 81 MHz, 25 °C) $\delta$P -19.78 (t, $J_{P-P}$ = 28 Hz, PMe$_3$), -5.02 (t, $J_{P-P}$ = 28 Hz, PMe$_3$).

2. Computational Details

All geometry optimizations were performed with the Gaussian09 package[7] at the PBE0 level.[8] Ti, Zr, Hf, Ta, Mo, W, Ru, Os, Rh, Ir, and Pt were represented by relativistic effective core potential (RECP) from the Stuttgart group and the associated basis set[9][11]. The remaining atoms (H, C, N, O, Cl and P) were represented by a triple-ζ pseeg-2 basis set.[12] NMR calculations were performed within the GIAO framework using ADF 2016[13] with the PBE0 functional and Slater-type basis sets of triple-ζ quality (TZ2P). Relativistic effects were treated by the 2 component zeroth order regular approximation (ZORA).[14][18] Analysis of scalar-relativistic natural localized molecular orbitals were done with the NBO 6.0 program.[19] Calculated NMR shielding tensors were analyzed using these scalar-relativistic NLMO.[20][23] The 3D representation of the calculated shielding tensors is obtained as polar plots[24][25] of functions $\sum_j r_i \sigma_{ij} r_j$, with scaling factors of 0.3 (Ti-ene and Ti-ene-PMe$_3$), 0.4 (alpha-carbon of Mo-CB and Ru-CB, beta-carbon of Ti-CB), 0.7 (Ti-Al-CB, alpha-carbon of Ti-CB, W-SP, beta-carbon of Mo-CB, W-TBP, W-SP, Ru-CB, Ru-TBP) or 1.0 (alpha-carbon of W-TBP and Ru-TBP).

Whenever possible, the geometry optimization and the calculation of the NMR shielding were carried out on a computational model that is identical to the experimental systems. For silica-supported systems the support was modeled by a OSi(OH)$_3$ ligand. The replacement of the experimental ligand by a simplified version for the NMR calculation in the case of Ta-TBP was carried out with a partial geometry optimization limited to an optimization of the simplified ligand in presence of the frozen position for all other atoms.

List of computational models not identical to the experimental system:

**W-TBP and W-SP**: The experimental system was grafted on a SiO$_2$-support. For the calculation the support was modeled by a OSi(OH)$_3$ ligand.

**Ta-TBP**: The experimental OAr ligand (Ar = 2,6-iPr-Ph) was replaced by OAr (Ar = Ph) for the NMR calculation.
3. All Calculated Compounds

Scheme S1. Drawings of all calculated compounds. Indices exp and calc are added to the name when the chemical shift tensor of the experimental system was measured by solid-state NMR and the calculated structure was truncated for NMR calculations.
4. Selected Structural Parameters of Metallacyclobutanes

Table S1. Calculated NMR signatures vs. structural parameters of metallacyclobutanes. Distances are given in Å, angles are given in degrees. Compounds reported to be active towards olefin metathesis are colored in green.

| Compound | \( \delta_{\text{iso}} \) | \( \Omega_{\text{ga}} \) | \( \delta_{\text{iso}}\gamma \) | \( \Omega_{\gamma} \) | \( M - C_{\alpha} \) | \( M - C_{\beta} \) | \( C_{\alpha} - C_{\beta} \) | \( \alpha_{\text{iso}} \) | \( \angle C_{\alpha} C_{\beta} C_{\gamma} \) |
|----------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Ti-CB    | 81              | 155             | 161             | 6               | 2.104           | 2.553           | 1.565           | 6.82            | 143.88          |
| Zr-CB    | 67              | 140             | 139             | 8               | 2.217           | 2.644           | 1.581           | 6.38            | 145.67          |
| Hf-CB    | 69              | 150             | 150             | 9               | 2.217           | 2.659           | 1.581           | 6.64            | 145.56          |
| Ti-Al-CB | 187             | 471             | 469             | -2              | 2.019           | 2.996           | 2.071           | 3.68            | 154.47          |
| Mo-CB    | -3              | 72              | 49              | 71              | 2.228           | 2.836           | 1.526           | 22.28           | 130.48          |
| W-CB     | -17             | 96              | 57              | 70              | 2.237           | 2.844           | 1.529           | 22.42           | 131.85          |
| Ta-TBP   | 90              | 166             | 194             | -2              | 2.111           | 2.430           | 1.585           | 1.70            | 147.19          |
| Mo-TBP   | 107             | 201             | 223             | -3              | 2.038           | 2.313           | 1.581           | 0.64            | 146.90          |
| Mo-SP    | 39              | 76              | 75              | 30              | 2.160           | 2.783           | 1.511           | 27.27           | 125.36          |
| W-TBP    | 102             | 197             | 222             | -6              | 2.050           | 2.346           | 1.586           | 1.06            | 147.52          |
| W-SP     | 44              | 46              | 66              | 26              | 2.159           | 2.747           | 1.518           | 26.66           | 128.67          |
| Ru-CB    | 100             | 231             | 218             | 1               | 1.94            | 2.231           | 1.582           | 0.01            | 144.03          |
| Ru-CB'   | 3               | 90              | 59              | 48              | 2.162           | 2.787           | 1.545           | 0.54            | 134.32          |
| Os-CB    | 5               | 91              | 61              | 47              | 2.160           | 2.787           | 1.539           | 1.28            | 134.69          |
| Rh-CB    | -21             | 99              | 22              | 30              | 2.077           | 2.707           | 1.525           | 1.24            | 128.96          |
| Ir-CB    | -11             | 109             | 53              | 46              | 2.133           | 2.745           | 1.539           | 13.09           | 134.69          |
| Pt-CB    | -7              | 68              | 26              | 27              | 2.033           | 2.648           | 1.529           | 6.47            | 127.04          |

Ligands: \( \text{X} = \text{OC} \left( \text{CF}_3 \right)_3, \text{Y} = \text{OSi} \equiv, \text{E} = \text{NAr} \) and \( \text{L}_1 = \text{IH}_2 \text{Mes} \) (see Scheme 1 and ESI Scheme S1).
5. $^{13}\text{C}\{^1\text{H}\}$ Solid-State NMR Spectra

Ti-CB

Figure S1. (a) The CP magic-angle turning\textsuperscript{26} (CP-MAT, 14.1 T at 100 K) spectrum of Ti-CB at a spinning rate of 4 kHz. The contact time for CP was 0.5 ms, and the recycle delay was 3.3 s. 56 scans per $t_1$ increment and 256 $t_1$ increments were acquired. (b-d) Blue: the spectra of the spinning side bands for the $\alpha$ and $\beta$ carbons in the metallacycle, which were obtained by slicing horizontally the CP-MAT spectrum at 86.8 ($\alpha$ carbon), 80.9 ($\alpha$ carbon), 6.1 ($\beta$ carbon) ppm, respectively. Red: best-fit simulated spinning side bands of the corresponding carbons.
Ti-ene-PMe₃

Figure S2. (a) Blue: The $^{13}$C{$^1$H} CPMAS (14.1 T at 100 K) spectrum of Ti-ene-PMe₃ recorded at a spinning rate of 11.5 kHz. The contact time for CP was 0.5 ms. Spinning side bands of Cp are marked with *. (b) Red: best-fit simulated spinning side bands of the methylidene carbon. Note that an unusually broad $^1$H NMR spectrum was observed ($\Omega \sim 200$ ppm), potentially indicating the presence of paramagnetic impurities in the sample.

Ti-Al-CB

Figure S3. (a) Blue: The $^{13}$C{$^1$H} CPMAS (9.4 T at room temperature) spectrum of Ti-Al-CB recorded at a spinning rate of 4 kHz. The contact time for CP was 0.5 ms. Spinning side bands of Cp and AlMe₂ are marked with *. (b) Red: best-fit simulated spinning side bands of the Ti-CH₂-Al carbon.
Figure S4. (a) The CP magic-angle turning\textsuperscript{[26]} (CP-MAT, 14.1 T at 100 K) spectrum of Ru-CB at a spinning rate of 4 kHz. The contact time for CP was 1 ms, and the recycle delay was set to 3.3 s. 56 scans per $t_1$ increment and 256 $t_1$ increments were acquired. (b-e) Blue: the spectra of the spinning side bands for the $\alpha$ and $\beta$ carbons in the metallacyclobutane, which were obtained by slicing horizontally the CP-MAT spectrum at 49.8 ($\beta$ carbon), 3.6 ($\alpha$ carbon), -1.0 ($\alpha$ carbon), -2.6 ppm ($\alpha$ carbon), respectively. Red: best-fit simulated spinning side bands of the corresponding carbons. The presence of 3 distinct signals for the $\alpha$-carbons suggests inequivalence between carbons in the solid-state for Ru-CB, which contains two molecules per unit cell and different orientation of PMe$_3$ (Figure S13).
6. NCS Analysis

Table S2: Calculated shielding tensor components of all investigated compounds in ppm.

|       | $\delta_{111}$ | $\delta_{222}$ | $\delta_{333}$ | $\delta_{111}$ | $\delta_{222}$ | $\delta_{333}$ |
|-------|----------------|----------------|----------------|----------------|----------------|----------------|
| Ti-CB | 110            | 30             | 114            | 185            | 81             | 161            |
|       | 152            | 170            | 233            | 6              | 39             | 21             |
|       | 124            | 128            | 192            | 67             | 139            | 62             |
|       | 182            | 173            | 224            | 8              | 41             | 18             |
|       | 122            | 41             | 133            | 190            | 69             | 150            |
|       | 182            | 174            | 219            | 9              | 39             | 16             |
| Ti-Al-CB | 3              | -279           | 96             | 192            | 187            | 469            |
| Ti-ene-PMe3 | -148          | -631           | 15             | 173            | 338            | 821            |
| Mo-CB | 193            | 156            | 197            | 228            | -3             | 35             |
|       | 141            | 101            | 151            | 172            | 49             | 90             |
|       | 207            | 161            | 204            | 257            | -17            | 30             |
|       | 134            | 101            | 129            | 171            | 57             | 89             |
| Ta-TBP | 101            | -4             | 143            | 162            | 90             | 194            |
| Mo-TBP | 84             | -32            | 115            | 168            | 107            | 223            |
| Mo-SP | 193            | 155            | 196            | 230            | -3             | 36             |
|       | 151            | 116            | 146            | 192            | 39             | 75             |
|       | 161            | 150            | 158            | 173            | 30             | 40             |
| W-TBP | 89             | -31            | 132            | 165            | 102            | 222            |
|       | 196            | 159            | 197            | 232            | -6             | 31             |
| W-SP  | 146            | 124            | 145            | 170            | 44             | 66             |
|       | 165            | 158            | 161            | 175            | 26             | 33             |
| Ru-TBP | 90             | -27            | 95             | 204            | 1<00           | 218            |
| Ru-CB | 188            | 149            | 201            | 217            | 1              | 41             |
|       | 143            | 106            | 159            | 164            | 48             | 85             |
| Ru-CB' | 185            | 130            | 205            | 221            | 5              | 61             |
| Os-CB | 223            | 170            | 235            | 263            | -32            | 20             |
|       | 150            | 106            | 164            | 181            | 40             | 84             |
| Rh-CB | 213            | 169            | 202            | 268            | -23            | 22             |
|       | 160            | 119            | 180            | 182            | 30             | 71             |
| Ir-CB | 200            | 138            | 217            | 247            | -10            | 53             |
|       | 145            | 110            | 158            | 167            | 46             | 81             |
| Pt-CB | 197            | 165            | 196            | 232            | -7             | 26             |

Table S3: NCS analysis of metallacyclobutanes (all values in ppm).

|       | $\delta_{\text{dia}}$ | $\delta_{\text{para}}$ | $\delta_{\text{dia}}$ | $\delta_{\text{para}}$ | $\delta_{\text{dia}}$ | $\delta_{\text{para}}$ |
|-------|------------------------|--------------------------|------------------------|--------------------------|------------------------|--------------------------|
| Ru-TBP | 220                    | -247                     | 238                    | -143                     | 220                    | -16                      |
| W-TBP  | 221                    | -72                      | 240                    | -39                      | 225                    | -8                       |
| W-SP   | 223                    | -255                     | 239                    | -107                     | 218                    | -53                      |
| Ti-CB  | 217                    | -57                      | 238                    | -40                      | 220                    | 11                       |
| Ti-Al-CB | 222               | -98                      | 235                    | -91                      | 214                    | -45                      |
| Ti-ene-PMe3 | 223            | -66                      | 218                    | -56                      | 228                    | -53                      |
| Ru-CB  | 219                    | -190                     | 233                    | -119                     | 224                    | -39                      |
| Mo-CB  | 235                    | -84                      | 243                    | -73                      | 232                    | 1                        |
Table S4: NCS analysis of metallacyclobutanes – $\sigma_{11}$ (all values in ppm).

|       | $\sigma_{1a}$ | $\sigma_{1a}$ | $\sigma_{1c}$ | $\sigma_{1c}$ | $\sigma_{1a}$ | $\sigma_{1a}$ | $\sigma_{1c}$ | $\sigma_{1c}$ |
|-------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| Ti-TBP | 220           | -247          | -121          | -79           | -25           | -24           |               |               |
| W-TBP  | 221           | -72           | -31           | -28           | -15           | 1             |               |               |
| W-SP   | 223           | -255          | -128          | -58           | -19           | -19           |               |               |
| Ti-CB  | 217           | -57           | -25           | -25           | -7            | -5            |               |               |
| Ti-ene | 222           | -98           | -86           | 7             | -12           | -2            |               |               |
| Ti-ene | 235           | -66           | -10           | 2             | -47           | 3             |               |               |
| Ti-CB  | 219           | -190          | -87           | -46           | -23           | -21           |               |               |
| Ru-CB  | 235           | -84           | 8             | 9             | -49           | -55           |               |               |
| Mo-CB  | 225           | -94           | -28           | -11           | -24           | -23           |               |               |
| Mo-CB  | 235           | -129          | -38           | -5            | -37           | -39           |               |               |
| Mo-CB  | 225           | -70           | -18           | -22           | -9            | -13           |               |               |
| Mo-CB  | 231           | -130          | -11           | -43           | -55           | -3            |               |               |
| Ti-Al-CB | 227          | -506          | -313          | -117          | -38           | -36           |               |               |
| Ti-ene-PMe$_3$ | 228      | -792          | -478          | -115          | -90           | -93           |               |               |
| Ti-ene | 231           | -861          | -512          | -141          | -94           | -96           |               |               |

Table S5: NCS analysis of metallacyclobutanes – $\sigma_{22}$ (all values in ppm).

|       | $\sigma_{1a}$ | $\sigma_{1a}$ | $\sigma_{1c}$ | $\sigma_{1c}$ | $\sigma_{1a}$ | $\sigma_{1a}$ | $\sigma_{1c}$ | $\sigma_{1c}$ |
|-------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| Ti-TBP | 238           | -143          | -16           | 12            | -71           | -71           |               |               |
| W-TBP  | 239           | -107          | -22           | 12            | -45           | -44           |               |               |
| W-SP   | 238           | -40           | -7            | 2             | -15           | -10           |               |               |
| Ti-CB  | 235           | -91           | -7            | 22            | -14           | -23           |               |               |
| Ti-CB  | 218           | -56           | -30           | 29            | -1            | 3             |               |               |
| Ti-CB  | 233           | -119          | -22           | 15            | -36           | -34           |               |               |
| Ru-CB  | 212           | -7            | -32           | 1             | 7             | 12            |               |               |
| Mo-CB  | 217           | -21           | -53           | -4            | 8             | 14            |               |               |
| Mo-CB  | 228           | -77           | -25           | -22           | 11            | -39           |               |               |
| Ti-Al-CB | 247          | -150          | -11           | -17           | -55           | -56           |               |               |
| Ti-ene-PMe$_3$ | 250      | -215          | -2            | -10           | -105          | -101          |               |               |
| Ti-ene | 254           | -239          | 0             | -6            | -114          | -111          |               |               |

Table S6: NCS analysis of metallacyclobutanes – $\sigma_{33}$ (all values in ppm).

|       | $\sigma_{1a}$ | $\sigma_{1a}$ | $\sigma_{1c}$ | $\sigma_{1c}$ | $\sigma_{1a}$ | $\sigma_{1a}$ | $\sigma_{1c}$ | $\sigma_{1c}$ |
|-------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| Ti-TBP | 220           | -16           | -16           | -14           | 6             | 4             |               |               |
| W-TBP  | 225           | -8            | -22           | 2             | 3             | 3             |               |               |
| W-SP   | 218           | -53           | -31           | -14           | 4             | 1             |               |               |
| W-SP   | 220           | 11            | -3            | 2             | 2             | 5             |               |               |
| Ti-CB  | 214           | -45           | -29           | -4            | 1             | 16            |               |               |
| Ti-CB  | 222           | -53           | -14           | -3            | -25           | 0             |               |               |
| Ti-CB  | 224           | -39           | -47           | -10           | 7             | 2             |               |               |
| Ru-CB  | 220           | 11            | -40           | 55            | -21           | -13           |               |               |
| Mo-CB  | 206           | -78           | -33           | -11           | -19           | -24           |               |               |
| Mo-CB  | 207           | 20            | 5             | -5            | 1             | 3             |               |               |
| Mo-CB  | 239           | -67           | -27           | -5            | -3            | -34           |               |               |
| Ti-Al-CB | 224          | -31           | -35           | -2            | 4             | 1             |               |               |
| Ti-ene-PMe$_3$ | 207      | -34          | -50           | 0             | 4             | 14            |               |               |
| Ti-ene | 205           | -32           | -52           | 1             | 11            | 9             |               |               |
7. Graphical Representation of the Results of the NCS Analysis

Figure S5. $\alpha$-carbons – $\sigma_{11}$ components (reproduction of Figure 2).

Figure S6. $\alpha$-carbons – $\sigma_{22}$ components.
Figure S7. $\alpha$-carbons – $\sigma_{33}$ components.

Figure S8. $\beta$-carbons – $\sigma_{11}$ components.
Figure S9. β-carbons – $\sigma_{22}$ components.

Figure S10. β-carbons – $\sigma_{33}$ components.
8. Graphical Representations of the Calculated Shielding Tensors

Representation as polar plots of functions $\Sigma_{\beta_i}c_{\beta_i}$.

**Figure S11.** Representation of all calculated shielding tensors.
**Figure S11.** Representation of all calculated shielding tensors (continued).
9. MO-Diagram of Cp₂TiCH₂CR₂CH₂ (Ti-CB)

Figure S12.A shows a qualitative MO diagram for Cp₂TiCH₂CR₂CH₂ developed from the Cp₂Ti⁺ and CH₂CR₂CH₂⁻ fragments. Three metal orbitals (labeled in C₂ᵥ point group) are available for making the bonds between the two fragments. Two orbitals are selected for the organic fragment: the out-of-phase combination of the two “lone pairs” mostly located on the two terminal carbons (blue orbital of b₂ symmetry) and the in-phase combination of two orbitals involved in the Cα-Cα' bonds (red orbital of a₁ symmetry). The bonding combination of the metal 1b₂ orbital with the blue orbital of the carbon chain yields the out-of-phase combination of the M-Cₐ and M-Cₐ' σ bonds, \{α(M-Cₐ) – α(M-Cₐ')\}; the corresponding calculated orbital is shown in Figure S12.C. The in-phase combination of the M-Cₐ and M-Cₐ' σ–bonds, which uses the 2a₁ metal orbital is not shown. The metal based 1a₁ orbital combines with the red orbital of CH₂CR₂CH₂⁻ to yield an occupied orbital that has local π-bonding character between the metal and the two α-carbons and is labeled \{π(M-Cₐ) + π(M-Cₐ')\}. The associated empty orbital with π-antibonding character between the metal and the two α-carbons is the LUMO and is labeled \{π*(M-Cₐ) + π*(M-Cₐ')\}(Figure S12.B).

![Diagram](image)

**Figure S12:** Schematic MO Diagram of Cp₂M(CH₂CH₂CH₂). B) Plot of the unoccupied orbital described as \{π*(M-Cₐ) + π*(M-Cₐ')\} and C) the occupied \{α(M-Cₐ) – α(M-Cₐ')\} orbital.
10. Reactivity of Ru-CB’ and Ru-CB

In the case of Ru-CB’, loss of a ligand creates a five-coordinated intermediate (Scheme S2), whose NMR chemical shifts are explored by computations. Ru-CB is selected as a model of the experimental system Ru-CB’. After loss of a PMe₃ ligand, the two resulting five-coordinated intermediates have square pyramidal geometries and calculated isotropic chemical shifts for the α- and β-carbons are within 10-55 ppm range as in the other square pyramid complexes (Scheme S2). Calculations show that the LUMO is oriented towards the empty coordination site and has no contribution on the α-carbon. This contrasts with the Ru-TBP complex where large deshielding at the α-carbons is observed and calculated. In Ru-TBP, the metal LUMO (green orbital in Figure 4B, main text) is correctly positioned to induce a π-type overlap at the α-carbon. Consequently, Ru-TBP is a metallacyclobutane active in olefin metathesis whereas (L₃)(PMe₃)Ru(CH₂CMe₂CH₂) undergoes β-methyl transfer after loss of PMe₃ (Scheme S2). This analysis shows how the d-orbital splitting associated with the ligand field and the electron count determine the main contributions to the paramagnetic term of the carbon chemical shift tensor and the reactivity of the metallacyclobutane.

Scheme S2. A) Products upon dissociation of a PMe₃ ligand from Ru-CB and the corresponding calculated isotropic chemical shifts. B) Known isoelectronic structure Ru-CB’ and reversible β-methyl transfer.
11. Phase Relationship of Orbitals in FCl and in Metallacyclobutanes

![Diagram of FCl and Metallacyclobutane Orbitals]

**Figure S13.** (A) Phase relationship in the HOMO of FCl (B) phase relationship of the occupied orbital in metathesis-active metallacyclobutanes, corresponding to the orbital shown in Figure S12(C).

12. Shielding Tensors of CH₂, CH₂²⁺, and Cp₂Ti(μ²-CH₂)₂TiCp₂

![Diagram of Carbon Shielding Tensors]

**Figure S14.** Calculated orientation of the carbon shielding tensor in (A) CH₂ and (B) bent CH₂²⁺.

**Figure S15.** Calculated orientation of the carbon shielding tensor in Cp₂Ti(μ²-CH₂)₂TiCp₂.
13. X-ray Crystallographic Analysis

Experimental

Single crystals of Ru-CB were grown from a saturated solution of Et$_2$O at -35 °C. A suitable crystal was selected and mounted on a Bruker SMART APEX CCD area detector diffractometer. The crystal was kept at 100 K during data collection. Using Olex2$^{[27]}$, the structure was solved with the XS$^{[28]}$ structure solution program using Direct Methods and refined with the XL$^{[29]}$ refinement package using Least Squares minimization.

Figure S16. The single crystal structure of Ru-CB with 50% thermal ellipsoids. All H-atoms are omitted for clarity. Selected bond distances (Å): Ru1–C1 = 2.169(3), C1–C2 = 1.548(5), C2–C3 = 1.539(5), Ru1–C3 = 2.183(3), Ru2–C18 = 2.186(3), C18–C19 = 1.549(5), C19–C20 = 1.547(5), Ru2–C20 = 2.179(3). Selected torsional angles (º): Ru1–C1–C2–C3 = 0.92, Ru2–C18–C19–C20 = 0.03.

Table S7. Crystal data and data collection parameters of Ru-CB.

| Property                                      | Value                  |
|-----------------------------------------------|------------------------|
| empirical formula                             | C$_{17}$H$_{46}$P$_4$Ru |
| formula weight                                | 475.49                 |
| crystal system                                | monoclinic             |
| a, Å                                         | 19.207(2)              |
| b, Å                                         | 9.4304(11)             |
| c, Å                                         | 26.475(3)              |
| α, deg.                                       | –                      |
| β, deg.                                       | 92.307(2)              |
| γ, deg.                                       | –                      |
| V, Å$^3$                                      | 4791.6(10)             |
| Z                                             | 8                      |
| Dcalcd, g/cm$^{-3}$                           | 1.318                  |
| μ [Mo-Kα], mm$^{-1}$                          | 0.919                  |
| T, K                                          | 100(2)                 |
| crystal size, mm                              | 0.22 × 0.18 × 0.15    |
| θ range for data collection (deg.)            | 1.286 to 26.372        |
| no. of reflections measured                   | 95015                  |
| unique data (Rint)                            | 0.0792                 |
| data / restraints / parameters                 | 9793 / 0 / 425         |
| $R1$ (I > 2.0σ(I))                            | 0.0391                 |
| $wR2$ (I > 2.0σ(I))                           | 0.0877                 |
| $R1$ (all data)                               | 0.0511                 |
| $wR2$ (all data)                              | 0.0920                 |
| GOF on $F^2$                                  | 1.119                  |
| Δρ, e Å$^{-3}$                                | 0.776, -0.387          |
14. Optimized Structures of all Calculated Species

Ti-CB

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | -0.028  | 0.012   | 0.483   |
| C    | 1.036   | -1.969  | 1.772   |
| C    | 0.991   | -3.415  | 1.174   |
| H    | -0.907  | -4.063  | -0.258  |
| H    | 0.412   | -3.919  | 0.906   |
| H    | 0.586   | -1.941  | -2.761  |
| H    | 2.051   | -1.585  | -1.841  |
| Ti   | -0.212  | -1.396  | -0.178  |
| C    | -0.380  | 0.357   | 1.456   |
| C    | 0.164   | -0.877  | 2.123   |
| C    | 1.118   | 0.453   | 0.538   |
| H    | -0.729  | 1.081   | 1.589   |
| C    | 1.328   | -1.521  | 1.654   |
| H    | -0.523  | -1.264  | 2.859   |
| C    | 1.916   | -0.701  | 0.678   |
| H    | 1.292   | 1.264   | -0.152  |
| H    | 1.694   | -2.476  | 1.990   |
| H    | 2.816   | -0.912  | 0.127   |
| C    | -2.010  | -1.927  | -1.683  |
| C    | -2.537  | -1.945  | -0.378  |
| C    | -1.955  | -0.615  | -1.974  |
| H    | -1.912  | -2.778  | -2.335  |
| C    | -2.439  | -0.647  | 0.144   |
| H    | -2.923  | -2.809  | 0.140   |
| C    | -1.854  | 0.179   | -0.845  |
| H    | -1.133  | -0.281  | -2.889  |
| H    | -2.748  | -0.338  | 1.130   |
| H    | -1.637  | 1.230   | -0.750  |
| C    | 2.381   | -3.824  | -0.691  |
| H    | 2.360   | -4.843  | -0.296  |
| H    | 3.095   | -3.791  | -1.518  |
| H    | 2.752   | -3.371  | 0.096   |
| C    | 0.571   | -4.402  | -2.263  |
| H    | 1.276   | -4.373  | -3.098  |
| H    | 0.542   | -5.420  | -1.865  |
| H    | -0.419  | -4.170  | -2.655  |

Zr-CB

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | 0.016   | -3.586  | 0.003   |
| C    | 1.099   | -2.030  | 1.836   |
| C    | 1.028   | -3.478  | 1.207   |
| H    | -0.851  | -4.185  | 0.272   |
| H    | 0.489   | -4.043  | 0.870   |
| H    | 0.653   | -2.021  | -2.830  |
| H    | 2.128   | -1.686  | 1.917   |
| Zr   | -0.217  | -1.388  | -0.171  |
| C    | 0.132   | 0.427   | 1.563   |
| C    | 0.258   | -0.803  | 2.241   |
| C    | 1.201   | 0.533   | 0.651   |
| H    | -0.656  | 1.149   | 1.703   |
| C    | 1.422   | -1.444  | 1.767   |
| H    | -0.416  | -1.187  | 2.992   |
| C    | 2.004   | -0.619  | 0.785   |
| H    | 1.377   | 1.352   | -0.030  |
| H    | 1.792   | -2.400  | 2.097   |
| H    | 2.902   | -0.828  | 0.227   |
| C    | -2.152  | -1.896  | -1.751  |
| C    | -2.684  | -1.928  | -0.447  |
| C    | -1.745  | 0.577   | -2.032  |
| H    | -2.055  | -2.741  | -2.414  |
| C    | -2.595  | -0.628  | 0.088   |
H -3.0730000000 -2.7980000000 0.0580000000
C -2.0130000000 0.2090000000 -0.8940000000
H -1.2880000000 -0.2340000000 -2.9470000000
H -2.9170000000 -0.3240000000 1.0720000000
H -1.8140000000 1.2640000000 -0.7910000000
C 2.4210000000 -3.8740000000 -0.7200000000
H 2.4100000000 -4.8910000000 -0.3180000000
H 3.1390000000 -3.8350000000 -1.5440000000
H 2.7790000000 -3.2100000000 0.0660000000
C 0.5970000000 -4.4620000000 -2.2930000000
H 1.2930000000 -4.4340000000 -3.1360000000
H 0.5640000000 -5.4810000000 -1.8990000000
H -0.3970000000 -4.2190000000 -2.6730000000

Hf-CB
C 0.0190000000 -3.5890000000 -0.0080000000
C 1.0970000000 -2.0400000000 -1.8370000000
C 1.0360000000 -3.4920000000 -1.2150000000
H -0.8490000000 -4.1870000000 -0.2870000000
H 0.4840000000 -4.0560000000 0.8580000000
H 0.6490000000 -2.0330000000 -2.8310000000
H 2.1250000000 -1.6960000000 -1.9290000000
Hf -0.2150000000 -1.3900000000 -0.1720000000
C 0.1250000000 0.4330000000 1.5650000000
C 0.2490000000 -0.7970000000 2.2420000000
C 1.1940000000 0.5390000000 0.6530000000
H -0.6640000000 1.1560000000 1.7040000000
C 1.4150000000 -1.4380000000 1.7700000000
H -0.4250000000 -1.1800000000 2.9940000000
C 1.9980000000 -0.6140000000 0.7900000000
H 1.3720000000 1.3580000000 -0.0270000000
H 1.7830000000 -2.3960000000 2.1000000000
H 2.8950000000 -0.8240000000 0.2310000000
C -2.1580000000 -1.8850000000 -1.7470000000
C -2.6860000000 -1.9190000000 -0.4420000000
C -1.7470000000 -0.5660000000 -2.0230000000
H -2.0610000000 -2.7280000000 -2.4120000000
C -2.5940000000 -0.6200000000 0.0970000000
H -3.0740000000 -2.7900000000 0.0620000000
C -2.0130000000 0.2180000000 -0.8830000000
H -1.2900000000 -0.2220000000 -2.9380000000
H -2.9150000000 -0.3180000000 1.0820000000
H -1.8110000000 1.2730000000 -0.7780000000
C 2.4280000000 -3.8810000000 -0.7230000000
H 2.4210000000 -4.8960000000 -0.3190000000
H 3.1490000000 -3.8410000000 -1.5430000000
H 2.7800000000 -3.2130000000 0.0640000000
C 0.6110000000 -4.4780000000 -2.3010000000
H 1.3080000000 -4.4500000000 -3.1430000000
H 0.5800000000 -5.4970000000 -1.9060000000
H -0.3830000000 -4.2380000000 -2.6830000000

Ti-Al-CB
Ti -0.1340000000 -0.1920000000 0.0940000000
Cl 0.9700000000 0.7350000000 -1.9680000000
Al -1.2800000000 1.1940000000 -2.3020000000
C -1.9780000000 0.2710000000 -0.5850000000
C -0.3920000000 1.9900000000 1.0240000000
C -0.8940000000 1.0470000000 1.9490000000
C 0.9900000000 1.7780000000 0.8930000000
C 0.1820000000 0.2490000000 2.3750000000
C 1.3490000000 0.6870000000 1.7030000000
C -0.3370000000 -2.1510000000 -1.2050000000
C 1.0100000000 -2.0910000000 -0.7840000000
Mo-CB
C 0.5770000000 -3.2480000000 0.0790000000
C 1.3540000000 -1.4930000000 -1.2030000000
C 1.2990000000 -3.0170000000 -1.2440000000
H -0.0860000000 -4.1130000000 0.1210000000
H 1.2990000000 -3.3490000000 0.8900000000
H 1.2830000000 -0.9730000000 -2.1590000000
H 2.2690000000 -1.1550000000 -0.7180000000
H 0.6320000000 -3.3240000000 -2.0560000000
C -0.2900000000 0.6620000000 1.5970000000
C -0.7400000000 -0.4260000000 2.3860000000
C 1.0120000000 0.3840000000 1.1430000000
H -0.8690000000 1.5360000000 1.3450000000
C 0.2750000000 -1.3960000000 2.4340000000
H -1.2820000000 -0.6350000000 -4.0080000000
H -1.6050000000 -0.8410000000 -3.9040000000
Mo -0.3460000000 -1.2230000000 0.2120000000
C 2.6070000000 -3.7880000000 -1.3950000000
H 2.3860000000 -4.8440000000 -1.1930000000
H 3.2910000000 -3.4680000000 -0.5990000000
C 3.3390000000 -3.7060000000 -2.7390000000
H 4.1370000000 -4.4580000000 -2.6950000000
C 4.0120000000 -2.3600000000 -2.9800000000
H 4.6140000000 -2.3880000000 -3.8920000000
H 3.2770000000 -1.5610000000 -3.0890000000
H 4.6710000000 -2.0930000000 -2.1510000000
C 2.4370000000 -4.0740000000 -3.9100000000
H 3.0120000000 -4.1520000000 -4.8350000000
H  1.9360000000 -5.0310000000 -3.7440000000
H  1.6660000000 -3.3170000000 -4.0670000000

W-CB
C  0.6110000000 -3.2890000000  0.0470000000
C  1.3780000000 -1.4990000000 -1.2000000000
C  1.3350000000 -3.0260000000 -1.2730000000
H  -0.0370000000 -4.1660000000  0.0660000000
H  1.3350000000 -3.4170000000  0.8520000000
H  1.3300000000 -0.9610000000 -2.1480000000
H  2.2960000000 -1.1870000000 -0.6980000000
H  0.6790000000 -3.3230000000 -2.1010000000
C  -0.0470000000  0.7410000000  1.4460000000
C  -0.7970000000 -0.2010000000  2.2010000000
C  1.2260000000  0.2020000000  1.2270000000
H  -0.4070000000  1.6830000000  1.0660000000
C  0.0090000000 -1.3460000000  2.4550000000
H  -1.8120000000 -0.0690000000  2.5370000000
C  1.2720000000 -1.0800000000  1.8310000000
H  2.0110000000  0.6630000000  0.6520000000
H  -0.2400000000 -2.1870000000  3.0780000000
H  2.1250000000 -1.7350000000  1.8250000000
C  -1.7560000000 -2.5680000000 -1.1490000000
C  -2.4480000000 -2.0940000000 -0.0050000000
C  -1.3270000000 -1.4740000000 -1.9190000000
H  -1.5600000000 -3.6010000000 -1.3770000000
C  -2.4560000000 -0.6640000000 -0.1090000000
H  -2.9530000000 -2.6970000000  0.7300000000
C  -1.7320000000 -0.2750000000 -1.2820000000
H  -0.7440000000 -1.5380000000 -2.8210000000
H  -2.9560000000  0.0130000000  0.5630000000
H  -1.6040000000  0.7240000000 -1.6650000000
C  2.6480000000 -3.7830000000 -1.4490000000
H  2.4530000000 -4.8360000000 -1.2140000000
H  3.3610000000 -3.4330000000 -0.6920000000
C  3.2930000000 -3.7060000000 -2.8290000000
H  4.0480000000 -4.4940000000 -2.9080000000
C  3.9470000000 -2.3730000000 -3.1610000000
H  4.4380000000 -2.4070000000 -4.1360000000
H  3.2230000000 -1.5590000000 -3.1780000000
H  4.7060000000 -2.1190000000 -2.4160000000
W  -0.3370000000 -1.2740000000  0.2190000000
H  2.5360000000 -3.9410000000 -3.5870000000

Ta-TBP
Ta  0.7510000000 -0.0360000000 -0.0070000000
C  -0.1740000000 -1.9120000000  0.2770000000
C  1.2870000000 -2.4040000000 -0.1090000000
C  2.3860000000 -1.2950000000 -0.3830000000
C  1.2200000000  0.4730000000  3.1360000000
C  0.0910000000  0.9470000000  3.8160000000
C  2.4920000000  0.4660000000  3.7290000000
C  0.2640000000  1.4040000000  5.1170000000
C  2.6100000000  0.9330000000  5.0300000000
C  1.5060000000  1.3970000000  5.7260000000
C  -0.0600000000  2.9850000000  0.4890000000
C  0.6840000000  3.8260000000  1.3330000000
C  -1.3880000000  3.2750000000  0.1520000000
C  0.0610000000  4.9550000000  1.8460000000
C  -1.9650000000  4.4220000000  0.6870000000
C  -1.2550000000  5.2570000000  1.5300000000
C  -0.1410000000  0.4280000000 -3.0440000000
C  -1.3720000000 -0.0120000000 -3.5540000000
C  0.6450000000  1.3700000000 -3.7230000000

S23
Mo-TBP

C  -1.1790000000  0.3180000000  -1.7850000000
C  -1.6040000000  -1.2090000000  -1.7550000000
C  -0.9050000000  -2.1790000000  -0.7210000000
Mo  -0.0010000000  -0.4120000000  -0.2910000000
C   2.2150000000   0.8480000000  1.5860000000
N   -1.1870000000   0.0180000000   0.9070000000
O    1.6400000000   0.0430000000   0.6710000000
O    1.2200000000  -0.8670000000  -1.7550000000
H   -0.6600000000   0.5770000000   2.7000000000
H   -0.2530000000   2.8930000000  -1.2110000000
H   -2.6650000000  -1.2300000000  -1.5290000000
H   -1.3690000000  -1.5990000000  -2.7400000000
C   -2.2100000000   0.3590000000  1.7510000000
C   -2.6780000000  -0.5930000000   2.6850000000
C   -3.7320000000  -0.2390000000   3.5140000000
C   -4.3110000000   1.0160000000   3.4460000000
C   -3.8300000000   1.9480000000   2.5420000000
C   -2.7800000000   1.6510000000   1.6870000000
H   -4.1060000000  -0.9600000000   4.2310000000
H   -5.1330000000   1.2710000000   4.1020000000
H   -4.2800000000   2.9320000000   2.5020000000
H   -2.0070000000   0.9720000000  -1.5480000000
C   -2.2820000000   2.7040000000   0.7290000000
H   -1.4300000000   2.2880000000   0.1940000000
C   -3.3540000000   3.0670000000  -0.2960000000
H   -3.7190000000   2.1860000000  -0.8270000000
H   -4.2150000000   3.5360000000   0.1860000000
H   -2.9580000000   3.7700000000  -1.0310000000
C   -1.7980000000   3.9500000000   1.4660000000
H   -1.0310000000   3.7030000000   2.1990000000
H   -1.3740000000   4.6650000000   0.7580000000
H   -2.6180000000   4.4460000000   1.9880000000
C   -2.0750000000  -1.9720000000   2.7850000000
H   -1.1940000000  -1.9930000000   2.1440000000
C   -3.0580000000  -3.0280000000   2.2830000000
H   -3.4070000000  -2.8040000000   1.2730000000
H   -2.5920000000  -4.0160000000   2.2760000000
H   -3.9380000000  -3.0780000000   2.9280000000
C   -1.6160000000  -2.2940000000   4.2050000000
H   -1.1180000000  -3.2650000000   4.2270000000
H   -0.9170000000  -1.5430000000   4.5730000000
H   -2.4590000000  -2.3410000000   4.8980000000
C   1.4500000000   0.8430000000   2.9520000000
C   3.6670000000   0.3060000000   1.8190000000
C   2.2890000000   2.3060000000   1.0270000000
H   -1.6040000000  -2.6260000000  -0.0280000000

S25
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| Mo      | -1.4830   | 0.5355    | 0.8340    |
| C       | 0.2230    | -1.3440   | 2.2580    |
| C       | -1.2810   | -1.4670   | 2.3300    |
| Mo      | 0.2900    | -0.4170   | 0.3140    |
| C       | 3.4550    | -1.0260   | 0.5490    |
| N       | -0.3230   | 1.1070    | 0.7590    |
| O       | -0.1420   | -0.9260   | -1.4560   |
| O       | 2.2160    | -0.5170   | 0.3770    |
| H       | -1.3190   | -2.5440   | 0.4430    |
| H       | -1.6650   | -2.3160   | 2.9060    |
| H       | -1.7260   | -0.5560   | 2.7350    |
| H       | 0.7000    | -2.3210   | 2.1550    |
| H       | 0.7490    | -0.7630   | 3.0160    |
| H       | -2.3920   | -1.1220   | 0.3970    |
| C       | -0.7240   | 2.4030    | 0.9760    |
| C       | -1.7610   | 2.9370    | 0.1860    |
| C       | -0.0890   | 3.1520    | 1.9850    |
| C       | -2.1620   | 4.2390    | 0.4440    |
| C       | -0.5270   | 4.4520    | 2.1960    |
| C       | -1.5540   | 4.9900    | 1.4390    |
| H       | -2.9600   | 4.6770    | 0.1400    |
| H       | -0.0600   | 5.0530    | 2.9650    |
| H       | -1.8830   | 6.0050    | 1.6230    |
| C       | 4.1680    | -0.2660   | 1.7120    |
| C       | 4.2320    | -0.8010   | -0.7930   |
| C       | 3.4070    | -2.5590   | 0.8660    |
| C       | 0.9950    | 2.5350    | 2.8310    |
| H       | 1.4360    | 1.7240    | 2.2500    |
| C       | -2.3560   | 2.1240    | 0.9350    |
| H       | -2.3260   | 1.0750    | 0.6330    |
| C       | -3.8050   | 2.4680    | 1.2440    |
| H       | -4.4270   | 2.4290    | 0.3480    |
| H       | -3.9040   | 3.4630    | 1.6840    |
| H       | -4.2010   | 1.7520    | 1.9650    |
| C       | -1.4930   | 2.2610    | 2.1900    |
| H       | -0.4600   | 1.9670    | 1.9960    |
| H       | -1.8880   | 1.6270    | 2.9860    |
| H       | -1.4890   | 3.2960    | 2.5400    |
| C       | 0.3870    | 1.9200    | 4.0910    |
| H       | -0.0590   | 2.6950    | 4.7180    |
| H       | -0.3920   | 1.1990    | 3.8430    |
| H       | 1.1550    | 1.4090    | 4.6760    |
| C       | 2.1150    | 3.5050    | 3.1820    |
| H       | 2.9200    | 2.9700    | 3.6870    |
| H       | 2.5290    | 3.9770    | 2.2900    |
| H       | 1.7760    | 4.2930    | 3.8580    |
| F       | 4.0150    | 0.4240    | -1.2510   |
F  3.6000000000  -0.7640000000  2.6460000000
F  0.3820000000  1.7360000000  2.8830000000
F  2.2070000000  1.3710000000  3.9580000000
F  0.9940000000  -0.2800000000  3.2980000000
F  2.6080000000  3.2220000000  1.8680000000
F  3.2070000000  2.3150000000  0.0080000000
F  1.1260000000  2.6140000000  0.4270000000
SL 2.2570000000  -0.7240000000  -2.9880000000
O  3.7720000000  -0.3180000000  -2.5280000000
H  3.8610000000  0.1420000000  -1.6940000000
O  1.5650000000  0.3630000000  -3.9970000000
H  1.9540000000  0.4580000000  -4.8650000000
O  2.3950000000  -2.1220000000  -3.8240000000
H  3.1200000000  -2.6910000000  -3.5680000000

W-SP
C  -1.5230000000  -1.5630000000  0.9150000000
C  0.2420000000  -1.3810000000  2.3330000000
C  -1.2700000000  -1.5100000000  2.4110000000
W  0.2500000000  -0.4520000000  0.3820000000
C  3.4300000000  -1.0460000000  0.4990000000
N  -0.3360000000  1.1150000000  0.8140000000
O  -0.1250000000  -0.9720000000  -1.4000000000
O  2.1790000000  -0.5450000000  0.3730000000
H  -1.3880000000  -2.5770000000  0.5220000000
H  -1.6410000000  -2.3670000000  2.9840000000
H  -1.7120000000  -0.6080000000  2.8390000000
H  0.7130000000  -2.3640000000  2.2420000000
H  0.7590000000  -0.8170000000  3.1100000000
H  -2.4590000000  -1.1610000000  0.5260000000
C  -0.7200000000  2.4230000000  0.9900000000
C  -1.7370000000  2.9560000000  0.1760000000
C  -0.0850000000  3.1920000000  1.9840000000
C  -2.1180000000  4.2720000000  0.3910000000
C  -0.5000000000  4.5050000000  2.1530000000
C  -1.5080000000  5.0410000000  1.3690000000
H  -2.9020000000  4.7070000000  -0.2140000000
H  -0.0280000000  5.1200000000  2.9080000000
H  -1.8190000000  6.0680000000  1.5200000000
C  4.1730000000  -0.2830000000  1.6410000000
C  4.1560000000  -0.8100000000  -0.8690000000
C  3.3990000000  -2.5800000000  0.8110000000
C  0.9770000000  2.5760000000  2.8610000000
H  1.4540000000  1.7830000000  2.2810000000
C  -2.3380000000  2.1230000000  -0.9280000000
H  -2.3270000000  1.0820000000  -0.5990000000
C  -3.7800000000  2.4810000000  -1.2540000000
H  -4.4070000000  2.4750000000  -0.3610000000
H  -3.8620000000  3.4660000000  -1.7200000000
H  -4.1850000000  1.7530000000  -1.9600000000
C  -1.4680000000  2.2160000000  -2.1820000000
H  -0.4390000000  1.9160000000  -1.9750000000
H  -1.8680000000  1.5680000000  -2.9650000000
H  -1.4490000000  3.2410000000  -2.5580000000
C  0.3310000000  1.9240000000  4.0830000000
H  -0.1550000000  2.6790000000  4.4706000000
H  -0.4250000000  1.1950000000  3.7880000000
H  1.0820000000  1.4140000000  4.6890000000
C  2.0660000000  3.5530000000  3.2780000000
H  2.8610000000  3.0170000000  3.8010000000
H  2.5060000000  4.0550000000  2.4150000000
H  1.6890000000  4.3180000000  3.9610000000
F  3.9120000000  0.4140000000  -1.3130000000
F  3.6970000000  -1.6690000000  -1.7790000000
F  5.4720000000  -0.9640000000  -0.7740000000
Ru-TBP
C -0.6570000000 0.0460000000 2.4640000000
C 1.9450000000 0.0240000000 1.7890000000
C 0.8520000000 0.0210000000 2.9330000000
H -1.1910000000 -0.8760000000 2.6890000000
H 2.5120000000 -0.9400000000 1.7320000000
H -1.1740000000 0.9710000000 2.7190000000
H 2.5290000000 0.9430000000 1.7580000000
H 1.0110000000 0.9290000000 3.5140000000
H 0.9890000000 -0.9080000000 3.4870000000
N -1.4540000000 0.2120000000 -1.6230000000
N 0.6500000000 -0.0110000000 -2.1770000000
Ru 0.2930000000 0.0590000000 0.7730000000
Cl 0.3170000000 2.4390000000 0.9040000000
Cl 0.3150000000 -2.3230000000 0.8190000000
C -0.2080000000 0.0900000000 -1.1570000000
C -1.4900000000 0.2860000000 -3.0900000000
C -0.0370000000 -0.0450000000 -3.4750000000
C -2.5760000000 0.4460000000 -0.7700000000
C -2.9610000000 1.7640000000 -0.4810000000
C -3.2500000000 -0.6610000000 -0.2330000000
C -3.9980000000 1.9530000000 0.4320000000
C -4.2820000000 -0.4180000000 0.6750000000
C -4.6540000000 0.8780000000 1.0340000000
C 2.0460000000 -0.2520000000 -1.9910000000
C 2.8980000000 0.8490000000 -1.8180000000
C 2.5210000000 -1.5720000000 -1.9650000000
C 4.2410000000 0.5960000000 -1.5350000000
C 3.8710000000 -1.7720000000 -1.6780000000
C 4.7400000000 -0.7040000000 -1.4450000000
C 2.3830000000 2.2540000000 -1.9300000000
C 1.6230000000 -2.7360000000 -2.2660000000
C 6.1940000000 -0.9520000000 -1.1500000000
C -2.3120000000 2.9370000000 -1.1560000000
C -2.8790000000 -2.0610000000 -0.6250000000
C -5.7320000000 1.1140000000 2.0560000000
H -1.7860000000 1.2910000000 -3.4060000000
H -2.2110000000 -0.4320000000 -3.4910000000
H 0.0590000000 -1.0390000000 -3.9220000000
H 0.4000000000 0.6880000000 -4.1580000000
H -4.2950000000 2.9690000000 0.6810000000
H -4.8090000000 -1.2660000000 1.1070000000
H 4.9110000000 1.4390000000 -1.3820000000
H 4.2490000000 -2.7900000000 -1.6280000000
H 1.7600000000 2.5160000000 -1.0680000000
H 3.2130000000 2.9630000000 -1.9830000000
H 1.7680000000 2.3820000000 -2.8280000000
H 1.5410000000 -2.8900000000 -3.3500000000
H 2.0230000000 -3.6540000000 -1.8300000000
H 0.6240000000 -2.5920000000 -1.8510000000
H 6.7630000000 -1.0960000000 -2.0770000000
H 6.6430000000 -0.1100000000 -0.6170000000
H 6.3290000000 -1.8520000000 -0.5430000000
H -2.4430000000 3.8430000000 -0.5620000000
H -1.1238000000 2.7860000000 -1.2790000000
H -2.7640000000 3.1150000000 -2.1410000000
H -2.7910000000 -2.1610000000 -1.7120000000
H -1.9150000000 -2.3480000000 -0.1920000000
H -3.6360000000 -2.7690000000 -0.2790000000
H -5.3000000000 1.2140000000 3.0590000000
H -6.2880000000 2.0330000000 1.8480000000
H -6.4430000000 0.2830000000 2.0870000000

Ru-CB
C 2.7370000000 -2.8310000000 0.6130000000
C 1.4170000000 -4.7930000000 0.8550000000
C 2.8930000000 -4.3580000000 0.7210000000
H 3.1530000000 -2.4360000000 -0.3160000000
H 3.2560000000 -2.3050000000 1.4170000000
C 1.8440000000 -2.2960000000 0.0600000000
H 2.8030000000 -2.7510000000 -2.3560000000
H 1.6290000000 -2.4410000000 -3.6510000000
H 1.9230000000 -1.2260000000 -2.3910000000
C 0.4610000000 -4.6990000000 -2.3380000000
H 1.3180000000 -5.2960000000 -2.0410000000
C -0.4390000000 -5.2240000000 -2.0260000000
H 0.4540000000 -4.5990000000 -3.4250000000
C 2.1700000000 -1.7150000000 3.7690000000
H 2.1060000000 -1.7030000000 4.8580000000
H 3.1190000000 -2.1580000000 3.4740000000
H 2.1540000000 -0.6890000000 3.4030000000
C 0.9300000000 -4.1930000000 4.0780000000
H 1.8170000000 -4.7590000000 3.8120000000
H 0.9850000000 -3.9170000000 5.1330000000
H 0.0680000000 -4.8370000000 3.9250000000
C -2.0220000000 -4.7070000000 2.2560000000
H -1.1893000000 -4.2990000000 3.2550000000
H -3.0520000000 -5.0550000000 2.1570000000
H -1.3450000000 -5.5550000000 2.1430000000
C -2.4340000000 -4.4650000000 -0.3910000000
H -2.4460000000 -3.9450000000 -1.3450000000
H -1.8900000000 -5.4020000000 -0.5090000000
H -3.4630000000 -4.6960000000 -0.1080000000
C 2.1400000000 0.2880000000 0.4090000000
H 2.0660000000 1.3750000000 0.3320000000
H 2.7470000000 0.0230000000 1.2740000000
H 2.6510000000 -0.1050000000 -0.4690000000

S30
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | -0.947  | 0.549   | 5.044   |
| H    | -0.767  | 1.110   | 5.966   |
| H    | -1.980  | 0.742   | 4.750   |
| H    | -0.865  | -0.511  | 5.287   |
| C    | 1.833   | -0.863  | 4.390   |
| H    | 2.545   | -0.564  | 5.166   |
| H    | 1.058   | -1.463  | 4.866   |
| H    | 2.366   | -1.510  | 3.692   |
| C    | 3.294   | 0.849   | 2.163   |
| H    | 3.535   | -0.215  | 2.165   |
| H    | 3.400   | 1.203   | 1.136   |
| H    | 4.051   | 1.358   | 2.767   |
| H    | 0.131   | -2.378  | 1.090   |
| H    | 1.985   | -1.032  | -0.781  |
| H    | 1.215   | 1.191   | -0.382  |
| Rh   | 0.068   | 0.278   | 1.787   |
| P    | -1.970  | -0.483  | 1.428   |
| C    | -3.332  | 0.721   | 1.599   |
| H    | -3.183  | 1.533   | 0.887   |
| H    | -4.304  | 0.257   | 1.425   |
| H    | -2.312  | 1.145   | 2.603   |
| C    | -2.498  | -1.795  | 2.584   |
| H    | -3.513  | -2.139  | 2.375   |
| H    | -1.806  | -2.634  | 2.500   |
| H    | -2.447  | -1.416  | 3.604   |
| C    | -2.382  | -1.254  | 0.173   |
| H    | -3.422  | -1.585  | 0.176   |
| H    | -2.229  | -0.542  | -0.983  |
| H    | -1.733  | -2.112  | -0.344  |

**Ir-CB**

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | 1.587   | -0.942  | -0.473  |
| C    | 0.735   | 0.340   | -0.449  |
| C    | 0.857   | -1.767  | 0.603   |
| H    | 0.087   | 0.418   | -1.325  |
| H    | 1.541   | -2.219  | 1.324   |
| H    | 0.269   | -2.577  | 0.162   |
| H    | 1.344   | 2.480   | -0.408  |
| Ir   | -0.284  | -0.131  | 1.365   |
| H    | 1.142   | 0.274   | 2.022   |
| P    | -0.901  | 2.049   | 1.691   |
| P    | -0.728  | 1.004   | 3.437   |
| P    | -2.204  | -0.870  | 0.301   |
| C    | 3.016   | -0.644  | 0.047   |
| H    | 3.603   | -1.564  | 0.028   |
| H    | 3.508   | 0.016   | -0.768  |
| H    | 3.026   | -0.152  | 0.928   |
| C    | 1.606   | -1.623  | -1.834  |
| H    | 2.055   | -0.976  | 2.594   |
| H    | 2.177   | -2.557  | -1.800  |
| H    | 0.593   | -1.870  | -2.164  |
| C    | 0.473   | 3.122   | 2.228   |
| H    | 1.295   | 3.005   | 1.521   |
| H    | 0.178   | 4.172   | 2.282   |
| H    | 0.824   | 2.788   | 3.204   |
| C    | -1.452  | 2.929   | 0.187   |
| H    | -2.406  | 2.522   | -0.152  |
| H    | -1.567  | 4.001   | 0.362   |
| H    | -0.715  | 2.763   | -0.599  |
| C    | 0.138   | -0.167  | 4.812   |
| H    | -0.194  | 0.870   | 4.874   |
| H    | -0.042  | -0.659  | 5.770   |
| H    | 1.206   | -0.163  | 4.593   |
| C    | -2.420  | -1.095  | 4.142   |
| H    | -3.044  | -1.747  | 3.530   |

S33
Pt-CB

C 1.3190000000 -1.2600000000 -0.7150000000
C 0.6980000000 0.1330000000 -0.6040000000
C 0.7750000000 -1.8790000000 0.5720000000
H -0.1200000000 0.3220000000 -1.2950000000
H 1.5320000000 -2.2340000000 1.2680000000
H -0.0070000000 -2.6200000000 0.4180000000
H 1.4150000000 0.9520000000 -0.6010000000
H 2.4080000000 -1.2110000000 -0.7020000000
H 1.0080000000 -1.7970000000 -1.6140000000
Cl 2.0150000000 0.4380000000 2.1470000000
Cl -2.0900000000 -0.7730000000 0.3460000000
N -0.8550000000 1.8860000000 1.7260000000
C -0.0560000000 2.9490000000 1.6520000000
C -2.1380000000 2.0600000000 2.0390000000
C -0.5130000000 4.2330000000 1.8880000000
H 0.9800000000 2.7440000000 1.4110000000
C -2.6720000000 3.3090000000 2.2980000000
H -2.7450000000 1.1640000000 2.0580000000
C -1.8450000000 4.4180000000 2.2200000000
H 0.1710000000 5.0680000000 1.8120000000
H -3.7190000000 3.4030000000 2.5510000000
H -2.2330000000 5.4100000000 2.4130000000
N -0.7490000000 -0.7990000000 3.2910000000
C -0.3350000000 -0.1660000000 4.3880000000
C -1.5500000000 -1.8560000000 3.4160000000
C -0.7150000000 -0.5620000000 5.6560000000
H 0.3370000000 0.6680000000 4.2260000000
C -1.9690000000 -2.3210000000 4.6490000000
H -1.8640000000 -2.3200000000 2.4900000000
C -1.5470000000 -1.6610000000 5.7910000000
H -0.3560000000 -0.0170000000 6.5190000000
H -2.6170000000 -3.1860000000 4.7030000000
H -1.8590000000 -2.0000000000 6.7710000000
Pt -0.0510000000 -0.1550000000 1.2640000000
15. References

[1] Yang, P.-H.; Liou, K.-F.; Lin, Y.-T., Ultrasonic irradiation in the synthesis of trimethylaluminum from methyl iodide via methyaluminum sesquioxide. J. Organomet. Chem. 1986, 307, 273.

[2] Kaleta, J.; Tarábek, J.; Akdag, A.; Pohl, R.; Michl, J., The 16 CB_{11}(CH_3)_6(CD_3)_{12-}{\eta}^* Radicals with 5-Fold Substitution Symmetry: Spin Density Distribution in CB_{11}Me_{12}{\eta}^*. Inorg. Chem. 2012, 51, 10819.

[3] Harney, M. B.; Keaton, R. J.; Sita, L. R., End-Group-Confined Chain Walking within a Group 4 Living Polyolefin and Well-Defined Cationic Zirconium Alkyl Complexes for Modeling This Behavior. J. Am. Chem. Soc. 2004, 126, 4536.

[4] Tebbe, F. N.; Parshall, G. W.; Reddy, G. S., Olefin homologation with titanium methylene compounds. J. Am. Chem. Soc. 1978, 100, 3611.

[5] Straus, D. A.; Grubbs, R. H., Titanacyclobutanes: substitution pattern and stability. Organometallics 1982, 1, 1658.

[6] Meinhart, J. D.; Anslyn, E. V.; Grubbs, R. H., Synthesis, reactivity and kinetic studies of bis(η^5-cyclopentadienyl)titanium methylenidene phosphine complexes. Organometallics 1989, 8, 583.

[7] 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.; Izmajlov, 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, J. A.; Peralta, Jr. 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.; Ylengar, 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, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09 (Gaussian, Inc., Wallingford CT, 2009) VERSION D.01.

[8] Adamo, C.; Barone, V., Toward reliable density functional methods without adjustable parameters: The PBE0 model. J. Chem. Phys. 1999, 110, 6158.

[9] Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H., Energy - adjusted ab initio pseudopotentials for the first row transition elements. J. Chem. Phys. 1987, 86, 866.

[10] Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H., Energy-adjustedab initio pseudopotentials for the second and third row transition elements. Theor. Chim. Acta 1990, 77, 123.

[11] Martin, J. M. L.; Sundermann, A., Correlation consistent valence basis sets for use with the Stuttgart–Dresden–Bonn relativistic effective core potentials: The atoms Ga–Kr and In–Xe. J. Chem. Phys. 2001, 114, 3408.

[12] Jensen, J., Unifying General and Segmented Contracted Basis Sets. Segmented Polarization Consistent Basis Sets. J. Chem. Theory Comput., 2014, 10, 1074.

[13] te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T., Chemistry with ADF. J. Comp. Chem. 2001, 22, 931. Amsterdam Density Functional (ADF) Theoretical Chemistry Vrieje Universitet see http://www.scm.com/ VERSION 2014.

[14] van Lenthe, E.; Baerends, E. J.; Snijders, J. G., Relativistic regular two-component Hamiltonians. J. Chem. Phys. 1993, 99, 4597.

[15] van Lenthe, E.; Baerends E. J.; Snijders, J. G., Relativistic total energy using regular approximations. J. Chem. Phys. 1994, 101, 9783.

[16] van Lenthe, E.; Baerends E. J.; Snijders, J. G., Geometry optimizations in the zero order regular approximation for relativistic effects. J. Chem. Phys. 1999, 110, 8943.
[17] van Lenthe, E.; Baerends, E. J.; Snijders, J. G., The zero - order regular approximation for relativistic effects: The effect of spin–orbit coupling in closed shell molecules. *J. Chem. Phys.* 1996, *105*, 6505.

[18] van Lenthe, E.; van Leeuwen, R.; Baerends, E. J.; Snijders, J. G., Relativistic regular two-component Hamiltonians. *Int. J. Quant. Chem.* 1996, *57*, 281.

[19] Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Landis, C. R.; Weinhold, F.; Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, USA 2013, [http://nbo6.chem.wisc.edu/](http://nbo6.chem.wisc.edu/)

[20] Bohmann, J. A.; Weinhold, F.; Farrar, T. C. J., Natural chemical shielding analysis of nuclear magnetic resonance shielding tensors from gauge-including atomic orbital calculations. *J. Chem. Phys.* 1997, *107*, 1173.

[21] Autschbach, J.; Zheng, T., Analyzing Pt chemical shifts calculated from relativistic density functional theory using localized orbitals: The role of Pt 5d lone pairs. *Magn. Reson. Chem.* 2008, *46*, S45.

[22] Autschbach, J., Analyzing NMR shielding tensors calculated with two-component relativistic methods using spin-free localized molecular orbitals. *J. Chem. Phys.* 2008, *128*, 164112.

[23] Aquino, F.; Pritchard, B.; Autschbach, J., Scalar Relativistic Computations and Localized Orbital Analyses of Nuclear Hyperfine Coupling and Paramagnetic NMR Chemical Shifts. *J. Chem. Theory Comput.* 2012, *8*, 598.

[24] a) Autschbach, J.; Zheng, S.; Shurko, R.W., Analysis of electric field gradient tensors at quadrupolar nuclei in common structural motifs. *Concepts in Magnetic Resonance Part A.* 2010, *36A*, 84.

[25] Zurek, E.; Pickard, C. J.; Autschbach, J., Density Functional Study of the $^{13}$C NMR Chemical Shifts in Single-Walled Carbon Nanotubes with Stone–Wales Defects. *J. Phys. Chem. C.* 2008, *112*, 11744.

[26] Bax, A.; Szeverenyi, N. M.; Maciel, G. E., Correlation of isotropic shifts and chemical shift anisotropies by two-dimensional fourier-transform magic-angle hopping NMR spectroscopy. *J. Magn. Reson.* 1983, *52*, 147.

[27] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* 2009, *42*, 339.

[28] XS, Sheldrick, G. M. *Acta Cryst.* 2008, *A64*, 112.

[29] XL, Sheldrick, G. M. *Acta Cryst.* 2008, *A64*, 112.