Manuscript Title:
Formation and Ligand-Based Reductivity of Bridged Bis-alkylidene Scandium(III) Complexes

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1) Experimental Details and Characterization Data

Unless otherwise noted, all reactions were conducted under slightly positive dry nitrogen pressure using standard Schlenk line techniques or under a nitrogen atmosphere in a Vigor (SG 1200/750TS-F) glovebox. The nitrogen in the glove box was constantly circulated through a copper/molecular sieves catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O2/H2O Combi-Analyzer to ensure both were always below 1 ppm. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Solvents were purified by an Mbraun SPS-800 Solvent Purification System and dried over fresh Na chips in a glovebox. Organometallic samples for NMR spectroscopic measurements were prepared in a glovebox by the use of J.Young valve NMR tubes (Wilmad 528-JY). 1H, and 13C NMR spectra were recorded on 400 MHz spectrometer (FT, 400 MHz for 1H; 100 MHz for 13C) at room temperature, unless otherwise noted. Mass spectra (MS) were recorded on a GC/MS spectrometer using an EI source. High-resolution mass spectra (HRMS) were recorded on FTMS mass spectrometer using an EI source or ESI source. Elemental analyses were performed on a Vario MICRO cube elemental analyzer.

**Note:** The signals of solvents in NMR spectra are due to the vapor of solvents in the glovebox. Because of the high sensitivity of these organometallics to air and moisture, some samples easily lost weight even in double layers of tin boats. Thus their elemental analysis data are not available.

1,4-Diiodo-1,3-butadienes 1a'-1c' and 1a-D10' were synthesized by the reported procedure.1,2 1c' and 1a-D10' are new compounds.

1c': Light yellow solid, isolated yield 64% (12.0 mmol scale, 5.5 g). 1H NMR (400 MHz, C6D6) δ 0.11 (s, 18H, Me3Si), 1.10 (s, 18H, 'Bu), 7.05 (d, J = 8.6 Hz, 4H, C6H5), 7.36 (d, J = 7.9 Hz, 4H, C6H5). 13C NMR (100 MHz, C6D6) δ 1.1, 31.3, 34.6, 112.6, 125.1, 129.6, 137.1, 151.7, 164.0. HRMS (ESI, m/z) calcd for C30H45I2Si2 [M + H]⁺: 715.1144, found 715.1140.

1a-D10': Light green solid, isolated yield 45% (30.0 mmol scale, 8.3 g). 1H NMR (400 MHz, THF-d8) δ -0.04 (s, 18H, Me3Si). 13C NMR (100 MHz, THF-d8) δ 1.0, 112.7, 128.1 (t, Jc-D = 24.1 Hz), 128.6 (t, Jc-D = 24.2 Hz), 129.7 (t, Jc-D = 24.2 Hz), 140.2, 164.3.
General Procedure for the Preparation of 1,4-Dilithio-1,3-butadienes 1a-c and 1a-D_{10}

{t}BuLi (4.0 mmol, 1.3 M in pentane) was added dropwise at -78 °C to a stirred solution of 1,4-diiodo-1,3-butadienes 1a'-c' and 1a-D_{10}' (1.0 mmol) in Et_{2}O (10 mL). After stirred at -78 °C for 1 h, the reaction mixture was allowed to warm to room temperature. The solvents were removed under vacuum in the glovebox and 1,4-dilithio-1,3-butadienes 1a-c were used for next step without further purification. The pure 1a-D_{10} was obtained by extracting the in situ-generated 1a-D_{10} with hexane and recrystallization in hexane after filtration of LiI.

1a-D_{10}: Red powder, isolated yield 98% (365.1 mg). 1H NMR (400 MHz, THF-d_{8}) δ -0.34 (s, 18H, Me_{3}Si). 13C NMR (100 MHz, THF-d_{8}) δ 3.1, 122.4 (t, J_{C-D} = 23.0 Hz), 126.0 (t, J_{C-D} = 23.1 Hz), 129.0 (t, J_{C-D} = 23.3 Hz), 154.0, 164.1, 208.1.

General Procedure for the Synthesis of Scandacyclopentadiene 2a and 2a-D_{10}

In the glovebox, ScCl_{3} (151.3 mg, 1.0 mmol) were dissolved in cold (-20 °C) THF solution (5 ml) in a 25 mL flask. And then the cold THF solution (10 mL) of 1,4-dilithio-1,3-butadiene 1a (362.5 mg, 1.0 mmol) was added dropwise into the above solution and stirred at -20 °C for 2 h. After the stirring is finished, the solvents were removed under reduced pressure. The residue was extracted with cold toluene for several times, LiCl was filtered and the volatiles of the filtrate were removed under reduced pressure to give dark yellow solids. Complex 2a could be isolated as yellow crystalline powder in good yield upon recrystallization of the saturated THF/Et_{2}O solution. The single crystals of 2a suitable for X-ray analysis could be obtained by volatilization of THF/Et_{2}O solution at -20 °C for 2 days.

2a: Yellow solid, isolated yield 65% (493.9 mg). 1H NMR (400 MHz, THF-d_{8}) δ -0.38 (s, 18H, Me_{3}Si), 6.55-6.57 (m, 4H, C_{6}H_{5}), 6.60-6.65 (m, 2H, C_{6}H_{5}), 6.69-6.72 (m, 4H, C_{6}H_{5}). 13C NMR (100 MHz, THF-d_{8}) δ 2.6, 26.4, 68.4, 123.9, 126.8, 129.9, 150.5 167.6, 203.8.

In the glovebox, ScCl_{3} (151.3 mg, 1.0 mmol) were dissolved in cold (-20 °C) THF solution (5 ml) in a 25 mL flask. And then the cold THF solution (10 mL) of deuterated 1,4-dilithio-1,3-butadiene 1a-D_{10} (372.5 mg, 1.0 mmol) was added dropwise into the above solution and stirred at -20 °C for 2 h. After the
stirring is finished, the solvents were removed under reduced pressure. The residue was extracted with cold toluene for several times, LiCl was filtered and the volatiles of the filtrate were removed under reduced pressure to give dark yellow solids. Complex 2a-D_{10} could be isolated as yellow crystalline powder in good yield upon recrystallization of the saturated THF/Et_{2}O solution.

![Diagram of 2a-D_{10}]

2a-D_{10}: Yellow solid, isolated yield 62% (477.3 mg). $^1$H NMR (500 MHz, THF-$d_8$) $\delta$ -0.37 (s, 18H, Me$_3$Si). $^{13}$C NMR (125 MHz, THF-$d_8$) $\delta$ 2.6, 123.4 (t, $J_{C-D} = 24.2$ Hz), 126.3 (t, $J_{C-D} = 24.4$ Hz), 129.4 (t, $J_{C-D} = 24.2$ Hz), 150.3 167.6, 203.8.

**General Procedure for the Syntheses of Organo-di-scandium complexes 3a-c**

In the glovebox, 1,4-dilithio-1,3-butadiene 1 (1.0 mmol) was dissolved in THF (10 mL) in a 25 mL sealed tube. Then THF suspension of ScCl$_3$ (151.3 mg, 1.0 mmol) was added at room temperature. And then the sealed tube was transferred outside of the glovebox and heated over 80 °C for 3 h in an oil bath (it is noteworthy that 2 could transform quantitatively into 3 at 45 °C for 3 h or 80 °C for 10 min in 0.05 mmol scale based on our in situ $^1$H NMR monitoring illustrated below, however, longer reaction time are required for complete transformation in 1.0 mmol scale). After the heat is finished, the sealed tube was transferred back to the glovebox and poured into a 25 ml flask. The solvents were removed under reduced pressure. The residue was extracted with toluene for several times, LiCl was filtered and the volatiles of the filtrate were removed under reduced pressure to give crimson solids. Complexes 3a-c could be isolated as red crystalline powder in general to good yields upon recrystallization of the saturated THF/Et$_2$O solution. The single crystals of 3a suitable for X-ray analysis could be obtained by volatilization of THF/Et$_2$O solution at room temperature for 1 day.

![Diagram of 3a]

3a: Red solid, isolated yield 62% (282.8 mg). $^1$H NMR (400 MHz, THF-$d_8$) $\delta$ -0.23 (s, 36H, Me$_3$Si), 6.67 (t, $J = 7.3$ Hz, 4H, C$_6$H$_5$), 6.78 (t, $J = 7.5$ Hz, 8H, C$_6$H$_5$), 7.52 (d, $J = 7.3$ Hz, 8H, C$_6$H$_5$). $^{13}$C NMR (100 MHz, THF-$d_8$) $\delta$ 5.2, 26.4, 68.3, 123.9, 126.5, 131.8, 134.4, 148.9.
3b: Red solid, isolated yield 75% (352.5 mg). $^1$H NMR (400 MHz, THF-$d^8$) $\delta$ -0.16 (s, 36H, Me$_3$Si), 2.09 (s, 12H, CH$_3$), 6.65 (d, $J = 7.9$ Hz, 8H, C$_6$H$_5$), 7.53 (d, $J = 7.9$ Hz, 8H, C$_6$H$_5$). $^{13}$C NMR (100 MHz, THF-$d^8$) $\delta$ 5.6, 21.3, 26.4, 68.3, 127.2, 132.1, 132.9, 135.4, 144.8.

3c: Red solid, isolated yield 68% (348.4 mg). $^1$H NMR (400 MHz, THF-$d^8$) $\delta$ -0.18 (s, 36H, Me$_3$Si), 1.12 (s, 36H, tBu), 6.82 (d, $J = 8.0$ Hz, 8H, C$_6$H$_5$), 7.51 (d, $J = 8.0$ Hz, 8H, C$_6$H$_5$). $^{13}$C NMR (100 MHz, THF-$d^8$) $\delta$ 5.5, 26.4, 31.9, 34.6, 68.4, 122.9, 131.8, 135.5, 144.9, 146.2.

General Procedure for the Synthesis of 6

In the glovebox, a THF solution (~10 mL) of tetramethylthiuram disulfide (480.8 mg, 2.0 mmol) and LiCl (42.4 mg, 1.0 mmol) was added to a solution of 3a (912.4 mg, 0.5 mmol) in THF (~10 mL) in a 25 mL sealed tube. And then the sealed tube was transferred outside of the glovebox and heated over 80 °C for 12 h in an oil bath. After the heat is finished, the sealed tube was transferred back to the glovebox and poured into a 25 ml flask. The solvent THF was removed under reduced pressure and hexane (~5 mL) was added to the residue. The mixture was stored at -20 °C overnight. Then the yellow solution was removed and the colourless powder was washed with cold hexane (~5 mL). The residual powder was dried under a vacuum. The single crystals suitable for X-ray analysis could be grown from THF/Hexane solution of 6 for 1 week.

6: Colourless solid, isolated yield 67% (509.6 mg). $^1$H NMR (400 MHz, THF-$d^8$) $\delta$ 3.40 (s, 6H, NMe$_2$). $^{13}$C NMR (100 MHz, THF-$d^8$) $\delta$ 26.4, 41.8, 68.2. It is noteworthy that 6 is sparingly soluble in THF-$d_8$, so the $^{13}$C NMR signals of amidinato carbon is not observable even after 12 h of measuring time. Anal. Calcd for C$_{11}$H$_{22}$Cl$_2$NO$_2$S$_2$Sc: C, 34.74; H, 5.83, N, 3.68. Found: C, 34.44; H, 5.87, N, 3.69.

General Procedure for the Synthesis of 7
In the glovebox, a THF solution (~10 mL) of cyclooctatetraene (104.2 mg, 1.0 mmol) was added to a solution of 3a (456.2 mg, 0.25 mmol) in THF (~10 mL) in a 25 mL sealed tube. And then the sealed tube was transferred outside of the glovebox and heated over 80 °C for 12 h in an oil bath. After the heat is finished, the sealed tube was transferred back to the glovebox and poured into a 25 ml flask. The solvent THF was removed under reduced pressure and hexane (~5 mL) was added to the residue. The mixture was stored at -20 °C overnight. Then the yellow solution was removed and the pale yellow powder was washed with cold hexane (~5 mL). The residual powder was dried under a vacuum. The single crystals suitable for X-ray analysis could be grown from DME (DME = 1,2-dimethoxyethane)/THF/Hexane solution of 7 for 3 days.

7: Pale yellow solid, isolated yield 85% (233.5 mg). $^1$H NMR (400 MHz, THF-d$_8$) $\delta$ 3.27 (s, 6H, OMe), 3.43 (s, 4H, CH$_2$), 6.53 (s, 8H, CH) $^{13}$C NMR (100 MHz, THF-d$_8$) $\delta$ 58.9, 72.7, 96.5.
2) Copies of $^1$H NMR and $^{13}$C NMR Spectra of All New Compounds
3) X-ray Crystallographic Studies

The single crystals of 2a, 3a, 6 and 7 suitable for X-ray analysis were grown as described in experimental section. The crystals were wrapped in mineral oil and then were frozen in low temperature. Data collections were performed on a SuperNova diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved with the shelxs-97 or Olex2 and refined with the XL refinement package using Least Squares minimization. Refinement was performed on $F^2$ anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Disordered solvent in 2a was squeezed by using Platon. Crystal data, data collection and processing parameters for 2a, 3a, 6 and 7 were summarized. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1555495 (2a), CCDC 1504242 (3a), 1519012 (6), CCDC 1539530 (7). Copies of these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The thermal ellipsoid plots were drawn by Ortep-3 v1.08.

SFigure 1. ORTEP drawing of 2a with 30% thermal ellipsoids. H atoms are omitted for clarity.

STable 1 Crystal data and structure refinement for 2a.

| Identification code | 2a |
|---------------------|----|
| Empirical formula   | $C_{38}H_{60}Cl_2LiO_4ScSi_2$|
| Formula weight      | 759.84 |
| Temperature/K       | 100.0(2) |
| Crystal system      | triclinic |
| Space group         | P-1 |
| a/Å                 | 12.55479(19) |
| b/Å                 | 13.3494(4) |
c/Å 14.7909(5)  
α/° 89.352(3)  
β/° 70.920(2)  
γ/° 89.305(2)  
Volume/Å³ 2342.52(11)  
Z 2  
ρcal cm/mg/m³ 1.077  
μ/mm⁻¹ 0.354  
F(000) 812.0  
Crystal size/mm³ 0.15 × 0.10 × 0.10  
Radiation MoKα (λ = 0.71073)  
2 θ range for data collection 7.098 to 52.044°  
Index ranges -17 ≤ h ≤ 8, -18 ≤ k ≤ 18, -20 ≤ l ≤ 20  
Reflections collected 67633  
Independent reflections 7818 [Rint = 0.0476, Rsigma = 0.0218]  
Data/restraints/parameters 7818/5/439  
Goodness-of-fit on F² 1.163  
Final R indexes [I>=2σ (I)] R1 = 0.0849, wR2 = 0.2402  
Final R indexes [all data] R1 = 0.0915, wR2 = 0.2498  
Largest diff. peak/hole / e Å⁻³ 1.02/-0.80

SFigure 2. ORTEP drawing of 3a with 30% thermal ellipsoids. H atoms, and two [Li(THF)₄]⁺ counterions are omitted for clarity.
Figure 3. ORTEP packing drawing of 3a with 30% thermal ellipsoids. H atoms, and C atoms of THF molecules of [Li(THF)₄]⁺ counterions are omitted for clarity. Colour code: Sc: violet red, C: black, Li: cyan, O: red, Cl: green, Si: orange. The a axis is across through the center of the μ₂-chloride bridges plane.

Table 2 Crystal data and structure refinement for 3a.

| Identification code  | 3a             |
|----------------------|----------------|
| Empirical formula    | C₈₄H₁₃₆Cl₂Li₁₀O₁₀Sc₄Si₄ |
| Formula weight       | 1824.70        |
| Temperature/K        | 180.00(10)     |
| Crystal system       | triclinic      |
| Space group          | P-1            |
| a/Å                  | 12.1887(6)     |
| b/Å                  | 12.7433(7)     |
| c/Å                  | 16.8304(10)    |
| α/°                  | 83.560(5)      |
| β/°                  | 75.676(5)      |
| γ/°                  | 74.313(5)      |
| Volume/Å³            | 2435.7(2)      |
| Z                    | 1              |
| ρcalc./mg/mm³        | 1.244          |
| μ/mm⁻¹               | 0.531          |
F(000) 968.0  
Crystal size/mm³ 0.05 × 0.05 × 0.05  
Radiation MoKα (λ = 0.71073)  
2 Θ range for data collection 5.722 to 52.044°  
Index ranges -14 ≤ h ≤ 15, -15 ≤ k ≤ 14, -13 ≤ l ≤ 20  
Reflections collected 16545  
Independent reflections 9579 [Rint = 0.0306, Rsigma = 0.0581]  
Data/restraints/parameters 9579/36/502  
Goodness-of-fit on F² 1.035  
Final R indexes [I>=2σ (I)] R₁ = 0.0609, wR₂ = 0.1443  
Final R indexes [all data] R₁ = 0.0888, wR₂ = 0.1668  
Largest diff. peak/hole / e Å⁻³ 1.08/-0.54

**Figure 4.** ORTEP drawing of 6 with 30% thermal ellipsoids. H atoms are omitted for clarity.

**Table 3 Crystal data and structure refinement for 6.**

| Identification code | 6  |
|---------------------|----|
| Empirical formula   | C₁₁H₂₂Cl₂NO₂S₂Sc |
| Formula weight      | 380.27 |
| Temperature/K       | 100.00(10) |
| Crystal system      | monoclinic |
| Space group         | P2₁/n |
| a/Å                 | 7.6252(3) |
| b/Å                 | 17.9614(5) |
| c/Å                 | 12.5733(4) |
| α°                  | 90 |
| β°                  | 101.302(3) |
Table 3 Crystal data and structure refinement for 7.

| Property                        | Value          |
|--------------------------------|----------------|
| Identification code            | 7              |
| Empirical formula              | C_{12}H_{18}ClO_{2}Sc |
| Formula weight                 | 274.67         |
| Temperature/K                  | 100.00(10)     |
| Crystal system                 | monoclinic     |
| Space group                    | Pn             |
| a/Å                            | 7.0301(3)      |
| b/Å                            | 10.1171(5)     |

Figure 5. ORTEP drawing of 7 with 30% thermal ellipsoids. H atoms are omitted for clarity.
c/Å 9.2007(4)
α/° 90
β/° 101.433(4)
γ/° 90
Volume/Å³ 641.41(5)
Z 2
ρ_{calc} mg/mm³ 1.422
μ/mm⁻¹ 0.765
F(000) 288.0
Crystal size/mm³ 0.15 × 0.14 × 0.12
Radiation MoKα (λ = 0.71073)
2 θ range for data collection 7.812 to 52.034°
Index ranges -8 ≤ h ≤ 8, -12 ≤ k ≤ 12, -11 ≤ l ≤ 11
Reflections collected 14657
Independent reflections 2510 [R_{int} = 0.0430, R_{sigma} = 0.0288]
Data/restraints/parameters 2510/2/147
Goodness-of-fit on F² 1.080
Final R indexes [I>2σ(I)] R₁ = 0.0400, wR₂ = 0.1167
Final R indexes [all data] R₁ = 0.0407, wR₂ = 0.1173
Largest diff. peak/hole / e Å⁻³ 0.72/-0.61
4) Mechanistic Investigations for the Formation of 3a

**In situ** $^1$H NMR Monitoring the Transformation from 2a to 3a and Alkyne. A J. Young valve NMR tube containing THF-$d_8$ solution of pure 2a (38.0 mg, 0.05 mmol) was injected into NMR spectrum spectrometer at 25 °C, and the $^1$H NMR spectra was recorded (SFigure 6 above). The $^1$H NMR spectra showed no obvious change for 2 weeks at 25 °C. When the NMR tube was heated over 80 °C for 10 min or 45 °C for 3 h in an oil bath, the peak at -0.38 ppm completely disappeared and two new singlets integrated to the same numbers of protons appeared at -0.23 ppm and 0.20 ppm (SFigure 6 bottom). The singlet at 0.20 ppm was assigned to the TMS proton resonance of Ph-C≡C-TMS by comparing with its standard spectrum. The GC retention time and molecular ion peak (m/z = 174) detected by GC-MS are also consistent with the standard sample of Ph-C≡C-TMS. The other new singlet at -0.23 ppm was assigned to the TMS groups of complex 3a.

SFigure 6. *In situ* $^1$H NMR spectra of the transformation from 2a (above) to 3a + alkyne (bottom). The transformation was observed by the signals of TMS groups of each compound.

**In situ** $^1$H NMR Monitoring the Transformation from 3a to 2a. A J. Young valve NMR tube containing THF-$d_8$ solution of pure 3a (36.5 mg, 0.02 mmol) with ferrocene as an internal standard was
injected into NMR spectrum spectrometer at 25 °C, and the ¹H NMR spectra was recorded (SFigure 7 above). When 2 equiv of hexachloroethane (9.5 mg, 0.04 mmol) were added into the NMR tube at 25 °C, the peak at -0.23 ppm completely disappeared and a new singlet appeared at -0.38 ppm which was assigned to the TMS signal of complex 2a (SFigure 7 bottom). The conversion ratio (70%) was based on the internal standard ferrocene. The formation of ScCl₃ can be characterized as ScCl₃(THF)₃ determined by X-ray analysis after post processing, cell parameters: a = 8.2062(6)Å, b = 12.5280(9)Å, c = 16.6537Å, α = 90°, β = 93.040(8)°, γ = 90°, its crystal structure have been already reported and thus its crystal structure is not illustrated. The formation of tetrachloroethylene can be identified by the ¹³C NMR spectrum and GC-MS.

SFigure 7. In situ ¹H NMR spectra of the transformation from 3a to 2a by adding hexachloroethane. The conversion ratio was based on the internal standard ferrocene.

In situ ¹H NMR Monitoring the Transformation from 3a to Alkyne. A J.Young valve NMR tube containing THF-d₈ solution of pure 3a (36.5 mg, 0.02 mmol) with ferrocene as an internal standard was injected into NMR spectrum spectrometer at 25 °C, and the ¹H NMR spectra was recorded (SFigure 8 above). When 4 equiv of hexachloroethane (19.0 mg, 0.08 mmol) were added into the NMR tube at 25 °C, and then the NMR tube was heated over 80 °C for 12 h in an oil bath. The peak at -0.23 ppm
completely disappeared and a new singlet appeared at 0.20 ppm which was assigned to the TMS signal of Ph-C≡C-TMS (SFigure 8 bottom). The conversion ratio (48%) was based on the internal standard ferrocene. The formation of ScCl$_3$ can be characterized as ScCl$_3$(THF)$_3$. The formation of tetrachloroethylene can be identified by the $^{13}$C NMR spectrum and GC-MS.

**SFigure 8.** *In situ* $^1$H NMR spectra of the transformation from 3a to Ph-C≡C-TMS by adding hexachloroethane. The conversion ratio was based on the internal standard ferrocene.

**The Crossover Reaction among 2a and 2a-D$_{10}$.** In the glovebox, 2a (38.0 mg, 0.05 mmol) and deuterated 2a-D$_{10}$ (38.5 mg, 0.05 mmol) were dissolved and mixed in THF (10 mL) in a 25 mL sealed tube. And then the sealed tube was transferred outside of the glovebox and heated over 80 ºC for 3 h in an oil bath. After the heating, the solution was cooled to the room temperature and quenched with excess H$_2$O. The solution was extracted with petroleum ether and dried over Na$_2$SO$_4$. The extract was directly used for high-resolution mass spectra (HRMS) on FTMS mass spectrometer using an EI source. The quenched product 4a, 4a-D$_5$, and 4a-D$_{10}$ could all be detected by HRMS (SScheme 1 and SFigure 9). **4a:** HRMS (EI, m/z) calcd for C$_{22}$H$_{32}$Si$_2$ [M$^+$]: 352.2037, found 352.2037; **4a-D$_5$:** HRMS (EI, m/z) calcd for
C_{22}H_{27}D_5Si_2 [M]^+: 357.2351, found 357.2352; 4a-D_{10}: HRMS (EI, m/z) calcd for C_{22}H_{22}D_{10}Si_2 [M]^+: 362.2665, found 362.2667. The detection of the crossover product 4a-D_5 by HRMS revealed that the 2-butene-1,1,4,4-tetraanion moiety in 3a should be originated from two molecules of scandacyclopentadienes instead of a simple reduction of a diene moiety in one scandacyclopentadiene.

Scheme 1. The crossover reaction among 2a and 2a-D_{10}.

Proposed Mechanisms for the Formation of 3a from 2a. Three possible mechanism pathways are illustrated in the Scheme 2. Pathway (a): cooperative intermolecular redox process. One molecule of scandacyclopentadiene 2a transfers its “ScCl” moiety to another molecule of 2a to generate 3a along with cleavage of β,β′-C−C bond of one molecule of scandacyclopentadiene to eliminate two equiv of alkyne; Pathway (b): stepwise intermolecular redox via scandacyclopropene. One molecule of 2a undergoes β,β′-C−C bond cleavage to generate the scandacyclopropene along with the elimination of...
one equiv of alkyne, and then the scandacyclopentene transfers its “ScCl” moiety to another molecule of 2a to generate 3a. *Pathway (c):* dimerization of scandacyclopentene via cooperative double metathesis. Two molecules of 2a will undergo β,β'-C–C bond cleavage to generate scandacyclopentene by release of two equiv of alkyne, and then two molecules of scandacyclopentene undergo dimerization to generate 3a.

**Scheme 2.** Proposed mechanisms for the formation of 3a from 2a.
5) Details of DFT Calculations

All calculations were carried out with the GAUSSIAN 09 program package. The optimization structure and correction energy of all the minima and transition states were fully calculated at the B3LYP level using the LANL2DZ (for Sc) and 6-31+G(d) (for other elements) in gas phase. The effect of solvent was examined by performing single-point self-consistent reaction field (SCRF) calculations based on the polarizable continuum model (PCM) for gas-phase optimized structures. THF was used as solvent, and solvation free energies ($\Delta G_{\text{sol}}$) were calculated at M06/SDD (for Sc)/ 6-311+G(d,p) (for other elements) level, by adding the solvation energies to the computed gas phase relative free energies ($\Delta G_{\text{gas}}$). Harmonic frequency calculations were performed at the same level for every structure to confirm it as a local minimum or transition state and to derive the thermochemical corrections for enthalpies and free energies. The intrinsic reaction coordinate (IRC) analysis was carried out throughout the pathways to confirm that all stationary points are smoothly connected to each other. The NBO analysis at B3LYP/SDD (for Sc)/ 6-311+G(d,p) (for other elements) level. All enthalpies and the Gibbs free energies in the text were given in Hartree. All distances were given in Å.

**IM1**

298K, 1 atm, gas phase
Thermal correction to Enthalpy = 0.714314 Hartree
Thermal correction to Gibbs Free Energy = 0.584531 Hartree
Sum of electronic and thermal Enthalpies = -2405.245457 Hartree
Sum of electronic and thermal Free Energies = -2405.375240 Hartree
298K, in THF
Sum of electronic and thermal Free Energies= 2404.997502 Hartree

| Standard orientation: |
|-----------------------|
| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
| Number          |              |            | X  | Y  | Z           |
| 1               | 6            | 0          | 0.192822 | 1.492350 | 0.204344 |
| 2               | 6            | 0          | -0.969422 | 0.784869 | 0.031567 |
| 3               | 6            | 0          | -1.013018 | -0.736917 | -0.139251 |
| 4               | 6            | 0          | 0.108827  | -1.503735 | -0.320727 |
| 5               | 21           | 0          | 1.695318  | -0.076377 | 0.135948 |
| 6               | 14           | 0          | 0.247522  | -3.345682 | -0.636895 |
| 7               | 14           | 0          | 0.457251  | 3.348441  | 0.236476  |
| 8               | 6            | 0          | 2.046611  | -3.869034 | -0.290302 |
| 9               | 1            | 0          | 2.205953  | -4.911124 | -0.599194 |
|   |   |   |   |   |   |
|---|---|---|---|---|---|
|10 |1 |0 | 2.774217 | -3.252569 |  -0.834497 |
|11 |1 |0 | 2.303410 | -3.809446 |   0.774763 |
|12 |6 |0 | -0.058201 | -3.742289 |  -2.477942 |
|13 |1 |0 |  0.200784 | -4.788844 |  -2.688837 |
|14 |1 |0 | -1.106131 | -3.596646 |  -2.764307 |
|15 |1 |0 |  0.560082 | -3.113728 |  -3.132647 |
|16 |6 |0 | -0.859911 | -4.472715 |   0.423354 |
|17 |1 |0 | -0.625662 | -5.527489 |   0.222328 |
|18 |1 |0 | -1.106131 | -3.596646 |  -2.764307 |
|19 |1 |0 | -1.925688 | -4.318252 |   0.224359 |
|20 |6 |0 |  0.322938 |  4.080168 |   1.991862 |
|21 |1 |0 |  1.042054 |  3.622651 |   2.682754 |
|22 |1 |0 |  0.539294 |  5.156844 |   1.964184 |
|23 |1 |0 | -0.680957 |  3.956202 |   2.415231 |
|24 |6 |0 |  2.246559 |  3.661399 |  -0.340916 |
|25 |1 |0 |  2.396115 |  3.334128 |  -1.378654 |
|26 |1 |0 |  2.486420 |  4.732518 |  -0.300695 |
|27 |1 |0 |  2.986112 |  3.135490 |   0.277317 |
|28 |6 |0 | -0.659400 |  4.372228 |  -0.915509 |
|29 |1 |0 | -0.319068 |  5.417248 |  -0.926062 |
|30 |1 |0 | -0.618592 |  4.003001 |  -1.948476 |
|31 |1 |0 | -1.709509 |  4.361913 |  -0.654811 |
|32 |6 |0 | -2.383350 | -1.365979 |  -0.068370 |
|33 |6 |0 | -3.043312 | -1.491749 |   1.165055 |
|34 |6 |0 | -3.014279 | -1.882422 |  -1.210244 |
|35 |6 |0 | -4.281524 | -2.130999 |   1.257791 |
|36 |1 |0 | -2.574766 | -1.092522 |   2.061632 |
|37 |6 |0 | -4.257303 | -2.515868 |  -1.124776 |
|38 |1 |0 | -2.527415 | -1.781704 |  -2.176719 |
|39 |6 |0 | -4.895502 | -2.646966 |   0.111857 |
|40 |1 |0 | -4.768561 | -2.225130 |   2.225727 |
|41 |1 |0 | -4.727130 | -2.905381 |  -2.025094 |
|42 |1 |0 | -5.860949 | -3.141633 |   0.181986 |
|43 |6 |0 | -2.299653 |  1.493277 |  -0.045961 |
|44 |6 |0 | -3.005876 |  1.590256 |  -1.255918 |
|45 |6 |0 | -2.841686 |  2.120296 |   1.086684 |
|46 |6 |0 | -4.200633 |  2.308351 |  -1.337176 |
|47 |1 |0 | -2.609619 |  1.106798 |  -2.145597 |
|48 |6 |0 | -4.043588 |  2.829925 |   1.014568 |
|49 |1 |0 | -2.314733 |  2.045446 |   2.034567 |
|50 |6 |0 | -4.726429 |  2.931686 |  -0.200753 |
|51 |1 |0 | -4.723072 |  2.379967 |  -2.288349 |
|52 |1 |0 | -4.445168 |  3.303647 |   1.907461 |
|53 |1 |0 | -5.658917 |  3.487070 |  -0.261861 |
|54 |17|0 |  4.110999 | -0.156498 |   0.580507 |
|55 |8 |0 |  2.184320 |  0.296321 |  -2.019966 |
Trimethylsilylphenylacetylene
298K, 1 atm, gas phase
Thermal correction to Enthalpy = 0.227889 Hartree
Thermal correction to Gibbs Free Energy = 0.169967 Hartree
Sum of electronic and thermal Enthalpies = -716.883619 Hartree
Sum of electronic and thermal Free Energies = -716.941540 Hartree
298K, in THF
Sum of electronic and thermal Free Energies= -716.6949 Hartree

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|------------------------|
| 1             | 6             | 0           | 3.877435 1.208669 0.000205 |
| 2             | 6             | 0           | 2.483163 1.214727 0.001851 |
| 3             | 6             | 0           | 1.765015 0.001506 0.001976 |
| 4             | 6             | 0           | 2.480254 -1.213449 0.000686 |
| 5             | 6             | 0           | 3.874526 -1.210792 -0.001010 |

S30
TS1

298K, 1 atm, gas phase
Thermal correction to Enthalpy = 0.712506 Hartree
Thermal correction to Gibbs Free Energy = 0.581805 Hartree
Sum of electronic and thermal Enthalpies = -2405.224408 Hartree
Sum of electronic and thermal Free Energies = -2405.355110 Hartree
298K, in THF
Sum of electronic and thermal Free Energies = -2404.976417 Hartree

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|--------------------------|
|               |               |             | X            | Y            | Z            |
| 1             | 6             | 0           | 1.418542     | 1.199993     | 0.461957     |
| 2             | 6             | 0           | 0.208890     | 1.378301     | 0.006524     |
| 3             | 6             | 0           | -1.355438    | -0.253441    | -0.193733    |
| 4             | 6             | 0           | -1.076377    | -1.468839    | -0.575987    |
| 5             | 21            | 0           | 0.874481     | -0.885972    | 0.209606     |
| 6             | 14            | 0           | -1.948549    | -3.025369    | -1.102180    |
| 7             | 14            | 0           | 2.982821     | 2.183067     | 0.693223     |
| 8             | 6             | 0           | -0.957646    | -4.549362    | -0.566011    |
| 9             | 1             | 0           | -1.378719    | -5.458799    | -1.015631    |
| 10            | 1             | 0           | 0.095044     | -4.477791    | -0.863442    |
|   |   |   |         |         |         |
|---|---|---|--------|--------|--------|
| 11| 1 | 0 | -0.975522 | -4.687033 | 0.522504 |
| 12| 6 | 0 | -2.038119 | -3.007806 | -3.00127 |
| 13| 1 | 0 | -2.517032 | -1.525851 | -3.373453 |
| 14| 1 | 0 | -2.617441 | -2.152851 | -3.373453 |
| 15| 1 | 0 | -1.036251 | -2.952309 | -3.446554 |
| 16| 6 | 0 | -3.704937 | -3.189208 | -0.397219 |
| 17| 1 | 0 | -4.159842 | -4.138083 | -0.713639 |
| 18| 1 | 0 | -3.694413 | -3.177773 | 0.700190 |
| 19| 1 | 0 | -4.360332 | -2.374382 | -0.724630 |
| 20| 6 | 0 | 3.210145  | 2.569276  | 2.539770 |
| 21| 1 | 0 | 3.309402  | 1.652187  | 3.132887 |
| 22| 1 | 0 | 4.120028  | 3.164016  | 2.696170 |
| 23| 1 | 0 | 2.366381  | 3.143663  | 2.943086 |
| 24| 6 | 0 | 4.457034  | 1.142998  | 0.109368 |
| 25| 1 | 0 | 4.399475  | 0.944106  | -0.968647 |
| 26| 1 | 0 | 5.403618  | 1.667433  | 0.296508 |
| 27| 1 | 0 | 4.497097  | 0.175371  | 0.624114 |
| 28| 6 | 0 | 2.986324  | 3.813194  | -0.280966 |
| 29| 1 | 0 | 3.949260  | 4.329518  | -0.164358 |
| 30| 1 | 0 | 2.831389  | 3.637503  | -1.35309 |
| 31| 1 | 0 | 2.195224  | 4.493883  | 0.053043 |
| 32| 6 | 0 | -2.590133 | 0.474629  | 0.132838 |
| 33| 6 | 0 | -2.763142 | 1.054909  | 1.401511 |
| 34| 6 | 0 | -3.659136 | 0.534154  | 0.779095 |
| 35| 6 | 0 | -3.973117 | 1.653393  | 1.756001 |
| 36| 1 | 0 | -1.937572 | 1.023670  | 2.107393 |
| 37| 6 | 0 | -4.863056 | 1.149618  | -0.432782 |
| 38| 1 | 0 | -3.536072 | 0.097901  | -1.766968 |
| 39| 6 | 0 | -5.027798 | 1.707808  | 0.839005 |
| 40| 1 | 0 | -4.090749 | 2.086066  | 2.746876 |
| 41| 1 | 0 | -5.673995 | 1.192418  | -1.156229 |
| 42| 1 | 0 | -5.966735 | 2.183422  | 1.10858 |
| 43| 6 | 0 | -0.528901 | 2.551570  | -0.487065 |
| 44| 6 | 0 | -1.033585 | 2.610800  | -1.797737 |
| 45| 6 | 0 | -0.679885 | 3.685841  | 0.332266 |
| 46| 6 | 0 | -1.639127 | 3.771199  | -2.282762 |
| 47| 1 | 0 | -0.946014 | 1.738944  | -2.439595 |
| 48| 6 | 0 | -1.301959 | 4.840320  | -0.144849 |
| 49| 1 | 0 | -0.305907 | 3.651958  | 1.352249 |
| 50| 6 | 0 | -1.779493 | 4.891676  | -1.458305 |
| 51| 1 | 0 | -2.010608 | 3.797179  | -3.304596 |
| 52| 1 | 0 | -1.411796 | 5.702138  | 0.509396 |
| 53| 1 | 0 | -2.259937 | 5.791923  | -1.832853 |
| 54| 17| 0  | 2.474560  | -2.632494 | 0.893625 |
| 55| 8 | 0  | 1.861752  | -0.982826 | -1.844303 |
| 56| 6 | 0  | 3.016391  | -1.783027 | -2.256154 |
# IM2

298K, 1 atm, gas phase

Thermal correction to Enthalpy = 0.483904 Hartree
Thermal correction to Gibbs Free Energy = 0.383249 Hartree
Sum of electronic and thermal Enthalpies = -1688.348108 Hartree
Sum of electronic and thermal Free Energies = -1688.448762 Hartree

298K, in THF
Sum of electronic and thermal Free Energies= -1688.285896 Hartree

### Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Å) |
|---------------|---------------|-------------|-----------------|
| 1             | 21            | 0           | \(1.089437, 0.012551, 0.380337\) |
| 2             | 17            | 0           | \(2.902172, -0.362839, 1.986653\) |
| 3             | 6             | 0           | \(-0.955620, 0.054695, -0.225233\) |
| 4             | 6             | 0           | \(-0.764315, -0.899907, 0.711486\) |
| 5             | 14            | 0           | \(-1.693642, -2.220577, 1.633651\) |
| 6             | 6             | 0           | \(-3.361484, -2.729134, 0.867093\) |
| 7             | 1             | 0           | \(-3.822700, -3.543967, 1.442714\) |
|    |    |    |          |          |          |
|----|----|----|----------|----------|----------|
|  8 | 1  | 0  | -4.071195| -1.894195|  0.836951|
|  9 | 1  | 0  | -3.233370| -3.083245| -0.164198|
| 10 | 6  | 0  | -1.990021| -1.625647|  3.416082|
| 11 | 1  | 0  | -2.443583| -2.417083|  4.027976|
| 12 | 1  | 0  | -1.045128| -1.333380|  3.891023|
| 13 | 1  | 0  | -2.660447| -0.756861|  3.445355|
| 14 | 6  | 0  | -0.599824| -3.775179|  1.700337|
| 15 | 1  | 0  | -1.073966| -4.574617|  2.285344|
| 16 | 1  | 0  | -0.410427| -4.171878|  0.693511|
| 17 | 1  | 0  |  0.371968| -3.551828|  2.158380|
| 18 | 6  | 0  | -2.170018|  0.548534| -0.883914|
| 19 | 6  | 0  | -3.329451|  0.887990| -0.151975|
| 20 | 6  | 0  | -4.459365|  1.415126| -0.780917|
| 21 | 1  | 0  | -3.330520|  0.737163|  0.924953|
| 22 | 6  | 0  | -3.339278|  1.270214| -2.913116|
| 23 | 6  | 0  | -4.476780|  1.601292| -2.167637|
| 24 | 1  | 0  | -5.334730|  1.671575| -0.187486|
| 25 | 1  | 0  | -3.336126|  1.412372| -3.991994|
| 26 | 1  | 0  | -5.359798|  2.002551| -2.658679|
| 27 | 8  | 0  |  2.076135| -0.943532| -1.350409|
| 28 | 6  | 0  |  3.482592| -1.373915| -1.361668|
| 29 | 6  | 0  |  1.371095| -1.489814| -2.512284|
| 30 | 6  | 0  |  3.679391| -2.055739| -2.715318|
| 31 | 1  | 0  |  4.101395| -0.487281| -1.209289|
| 32 | 1  | 0  |  3.622902| -2.051689| -0.516015|
| 33 | 6  | 0  |  2.276647| -2.603743| -3.027523|
| 34 | 1  | 0  |  0.386790| -1.812788| -2.171962|
| 35 | 1  | 0  |  1.256171| -0.680298| -3.242217|
| 36 | 1  | 0  |  4.444817| -2.836229| -2.667156|
| 37 | 1  | 0  |  3.983913| -1.327698| -3.476905|
| 38 | 1  | 0  |  2.092027| -3.533154| -2.476168|
| 39 | 1  | 0  |  2.119332| -2.800380| -4.092586|
| 40 | 6  | 0  | -2.200101|  0.773622| -2.277185|
| 41 | 1  | 0  | -1.310006|  0.547894| -2.861471|
| 42 | 8  | 0  |  1.218223|  2.237638|  0.546611|
| 43 | 6  | 0  |  0.109908|  3.173558|  0.336005|
| 44 | 6  | 0  |  2.398029|  2.954682|  1.039098|
| 45 | 6  | 0  |  0.555882|  4.473176|  1.002372|
| 46 | 1  | 0  | -0.030117|  3.282728| -0.744183|
| 47 | 1  | 0  | -0.786726|  2.724559|  0.762764|
| 48 | 6  | 0  |  2.082396|  4.432608|  0.822242|
| 49 | 1  | 0  |  2.527601|  2.697360|  2.094115|
| 50 | 1  | 0  |  3.264152|  2.591146|  0.481840|
| 51 | 1  | 0  |  0.295146|  4.468975|  2.067510|
| 52 | 1  | 0  |  0.090105|  5.349738|  0.541318|
| 53 | 1  | 0  |  2.618057|  5.072033|  1.530850|
THF
298K, 1 atm, gas phase
Thermal correction to Enthalpy = 0.121427 Hartree
Thermal correction to Gibbs Free Energy = 0.090240 Hartree
Sum of electronic and thermal Enthalpies = -232.332920 Hartree
Sum of electronic and thermal Free Energies = -232.364106 Hartree
298K, in THF
Sum of electronic and thermal Free Energies = -232.2554 Hartree

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|------------------------|
|               |               |             | X          | Y          | Z          |
| 1             | 6             | 0           | 1.187429   | -0.461502 | 0.000000  |
| 2             | 8             | 0           | 0.000012   | -1.258210 | -0.000001 |
| 3             | 6             | 0           | -1.187420  | -0.461523 | 0.000000  |
| 4             | 6             | 0           | -0.774622  | 1.027075  | 0.000000  |
| 5             | 6             | 0           | 0.774604   | 1.027086  | 0.000000  |
| 6             | 1             | 0           | 1.777788   | -0.723826 | 0.887630  |
| 7             | 1             | 0           | 1.777788   | -0.723825 | -0.887631 |
| 8             | 1             | 0           | -1.777778  | -0.723858 | -0.887629 |
| 9             | 1             | 0           | -1.777778  | -0.723859 | 0.887628  |
| 10            | 1             | 0           | -1.170597  | 1.543548  | -0.880252 |
| 11            | 1             | 0           | -1.170597  | 1.543547  | 0.880254  |
| 12            | 1             | 0           | 1.170567   | 1.543569  | -0.880252 |
| 13            | 1             | 0           | 1.170567   | 1.543568  | 0.880253  |

IM3
298K, 1 atm, gas phase
Thermal correction to Enthalpy = 0.719475 Hartree
Thermal correction to Gibbs Free Energy = 0.578970 Hartree
Sum of electronic and thermal Enthalpies = -2912.031003 Hartree
Sum of electronic and thermal Free Energies = -2912.171507 Hartree
298K, in THF
Sum of electronic and thermal Free Energies = -2912.069630 Hartree

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|------------------------|
|               |               |             | X          | Y          | Z          |
| 1             | 21            | 0           | 0.320666   | 1.092053  | -0.885919 |

S35
|   |     |   | 0.726158  | 2.452236  | -2.810488  |
|---|-----|---|----------|-----------|-------------|
| 2 | 17  | 0 | 1.586102 | -0.806652 | -0.621535   |
| 3 | 6   | 0 | 2.171921 | 0.329765  | -0.175230   |
| 4 | 6   | 0 | -1.742070| 0.042741  | 0.242500    |
| 5 | 6   | 0 | -1.789598| -0.018917 | -1.109209   |
| 6 | 21  | 0 | -0.517027| -1.690244 | -0.322670   |
| 7 | 14  | 0 | -3.003284| 0.374830  | -2.508608   |
| 8 | 14  | 0 | -3.003284| 0.374830  | -2.508608   |
| 9 | 6   | 0 | -4.447602| -0.862153 | -2.472240   |
| 10| 1   | 0 | -4.997282| -0.809937 | -3.421966   |
| 11| 1   | 0 | -4.082659| -1.889394 | -2.354215   |
| 12| 1   | 0 | -5.163542| -0.657641 | -1.667604   |
| 13| 1   | 0 | -2.123019| 0.159069  | -4.168124   |
| 14| 6   | 0 | -2.812310| 0.363308  | -4.998664   |
| 15| 1   | 0 | -1.264776| 0.832638  | -4.269948   |
| 16| 1   | 0 | -1.760454| -0.870331 | -4.283589   |
| 17| 6   | 0 | -4.082659| -1.889394 | -2.354215   |
| 18| 1   | 0 | -4.420194| 2.340930  | -3.159882   |
| 19| 6   | 0 | -4.149484| 2.334184  | -1.407019   |
| 20| 1   | 0 | -2.868441| 2.884867  | -2.510282   |
| 21| 6   | 0 | -2.284260| -3.884018 | -0.232006   |
| 22| 6   | 0 | -3.672769| 2.150100  | -2.377810   |
| 23| 6   | 0 | -3.003284| 0.374830  | -2.508608   |
| 24| 1   | 0 | -3.554638| -0.728699 | 0.820449    |
| 25| 6   | 0 | -1.974500| -2.639509 | -3.042641   |
| 26| 1   | 0 | 2.119653 | -1.753333 | -3.673089   |
| 27| 6   | 0 | 2.540075 | -3.466811 | -3.492601   |
| 28| 1   | 0 | 0.912534 | -2.909915 | -3.082417   |
| 29| 1   | 0 | 4.448424 | -2.011705 | -1.349654   |
| 30| 1   | 0 | 4.918544 | -2.860926 | -1.864992   |
| 31| 1   | 0 | 4.690107 | -1.103873 | -1.913800   |
| 32| 1   | 0 | 4.908730 | -1.919138 | 0.360973    |
| 33| 1   | 0 | -3.694877| 0.527158  | 1.257967    |
| 34| 6   | 0 | -2.243553| 1.271877  | 2.368020    |
| 35| 1   | 0 | -4.068136| 0.207489  | 1.204710    |
| 36| 6   | 0 | -3.126333| 1.714732  | 3.355277    |
| 37| 6   | 0 | -1.184797| 1.509191  | 2.438566    |
| 38| 6   | 0 | -4.946819| 0.622313  | 2.207571    |
| 39| 1   | 0 | -4.439180| -0.387112 | 0.376279    |
| 40| 6   | 0 | -4.484956| 1.387606  | 3.283781    |
| 41| 1   | 0 | -2.751691| 2.303326  | 4.190200    |
| 42| 1   | 0 | -5.998544| 0.352119  | 2.144519    |
| 43| 1   | 0 | -5.171656| 1.717073  | 4.059240    |
| 44| 6   | 0 | 3.501676 | 0.681031  | 0.318435    |
| 45| 6   | 0 | 4.031156 | 0.091680  | 1.485874    |
| 46| 6   | 0 | 4.254876 | 1.698977  | -0.306628   |

S36
|   |   |   |   |   |   |
|---|---|---|---|---|---|
| 48 | 6 | 0 | 5.265806 | 0.493832 | 2.000224 |
| 49 | 1 | 0 | 3.462101 | -0.687557 | 1.988440 |
| 50 | 6 | 0 | 5.503167 | 2.074747 | 0.189908 |
| 51 | 1 | 0 | 3.855123 | 2.176834 | -1.198421 |
| 52 | 6 | 0 | 6.013541 | 1.481832 | 1.351530 |
| 53 | 1 | 0 | 5.650445 | 0.025665 | 2.903795 |
| 54 | 1 | 0 | 6.076344 | 2.842210 | -0.325346 |
| 55 | 1 | 0 | 6.979193 | 1.787334 | 1.745908 |
| 56 | 17 | 0 | -1.500123 | -3.614127 | -1.374683 |
| 57 | 8 | 0 | 0.147230 | 2.844685 | 0.473374 |
| 58 | 6 | 0 | -0.807129 | 3.917666 | 0.175858 |
| 59 | 6 | 0 | 1.211655 | 3.338881 | 1.346194 |
| 60 | 6 | 0 | -0.135670 | 5.194196 | 0.677412 |
| 61 | 1 | 0 | -0.987674 | 3.909535 | -0.901287 |
| 62 | 1 | 0 | -1.732800 | 3.689596 | 0.714514 |
| 63 | 6 | 0 | 0.707315 | 4.685913 | 1.858958 |
| 64 | 1 | 0 | 1.373709 | 2.587923 | 2.122585 |
| 65 | 1 | 0 | 2.123023 | 3.434922 | 0.749433 |
| 66 | 1 | 0 | -0.868814 | 5.953226 | 0.967125 |
| 67 | 1 | 0 | 0.508510 | 5.617223 | -0.101703 |
| 68 | 1 | 0 | 0.081693 | 5.617223 | 2.749890 |
| 69 | 1 | 0 | 1.532538 | 5.356572 | 2.117650 |
| 70 | 8 | 0 | -0.448506 | -2.543542 | 1.741016 |
| 71 | 6 | 0 | -0.124362 | -1.772011 | 2.941990 |
| 72 | 6 | 0 | -0.857076 | -3.903524 | 2.109696 |
| 73 | 6 | 0 | -0.136862 | -2.782734 | 4.089134 |
| 74 | 1 | 0 | 0.845797 | -1.296017 | 2.778256 |
| 75 | 1 | 0 | -0.893597 | -1.903539 | 3.051986 |
| 76 | 6 | 0 | -1.157398 | -3.825184 | 3.602758 |
| 77 | 1 | 0 | -1.705644 | -4.171320 | 1.479724 |
| 78 | 1 | 0 | -0.019683 | -4.574785 | 1.890243 |
| 79 | 1 | 0 | -0.417886 | -2.315573 | 5.038026 |
| 80 | 1 | 0 | 0.850878 | -3.242273 | 4.214320 |
| 81 | 1 | 0 | -2.181113 | -3.471000 | 3.771136 |
| 82 | 1 | 0 | -1.045521 | -4.797106 | 4.093283 |

**TS2**

298K, 1 atm, gas phase
Thermal correction to Enthalpy = 0.718139 Hartree
Thermal correction to Gibbs Free Energy = 0.580535 Hartree
Sum of electronic and thermal Enthalpies = -2912.009940 Hartree
Sum of electronic and thermal Free Energies = -2912.147544 Hartree

298K, in THF
Sum of electronic and thermal Free Energies = -2912.054464 Hartree

Standard orientation:

S37
| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|------------------------|
| 1             | 21            | 0           | -1.519312 0.023678 -0.995532 |
| 2             | 17            | 0           | -2.826119 0.069700 -3.029487 |
| 3             | 6             | 0           | -0.012534 1.621179 -0.733208 |
| 4             | 6             | 0           | -0.374811 1.128588 0.500826 |
| 5             | 6             | 0           | 0.374884 -1.128572 0.500803 |
| 6             | 6             | 0           | 0.012393 -1.621206 -0.733150 |
| 7             | 21            | 0           | 1.519132 -0.023717 -0.995785 |
| 8             | 14            | 0           | -0.356189 -3.305727 -1.487491 |
| 9             | 14            | 0           | 0.355945 3.305670 -1.487669 |
| 10            | 6             | 0           | 0.706583 -4.634595 -0.638425 |
| 11            | 1             | 0           | 0.527894 -5.617988 -1.094014 |
| 12            | 1             | 0           | 1.775003 -4.408913 -0.750051 |
| 13            | 1             | 0           | 0.493030 -4.715835 0.433787 |
| 14            | 6             | 0           | 0.085244 -3.236193 -3.324279 |
| 15            | 1             | 0           | -0.066608 -4.214244 -3.800556 |
| 16            | 1             | 0           | -0.543301 -2.506178 -3.849387 |
| 17            | 1             | 0           | 1.128942 -2.938689 -3.481340 |
| 18            | 6             | 0           | -2.187475 -3.830063 -1.379525 |
| 19            | 1             | 0           | -2.315455 -4.819001 -1.841390 |
| 20            | 1             | 0           | -2.560492 -3.901049 -0.350058 |
| 21            | 1             | 0           | -2.829589 -3.132710 -1.932694 |
| 22            | 6             | 0           | 2.187292 3.829911 -1.380144 |
| 23            | 1             | 0           | 2.829235 3.132489 -1.933429 |
| 24            | 1             | 0           | 2.315228 4.818821 -1.842081 |
| 25            | 1             | 0           | 2.560553 3.900922 -0.350765 |
| 26            | 6             | 0           | -0.085917 3.236116 -3.324354 |
| 27            | 1             | 0           | -1.129654 2.938614 -3.481166 |
| 28            | 1             | 0           | 0.065831 4.214164 -3.800672 |
| 29            | 1             | 0           | 0.542500 2.506094 -3.849609 |
| 30            | 6             | 0           | -0.706571 4.634619 -0.638400 |
| 31            | 1             | 0           | -0.527950 5.617986 -1.094078 |
| 32            | 1             | 0           | -1.775029 4.408973 -0.749760 |
| 33            | 1             | 0           | -0.492760 4.715904 0.433756 |
| 34            | 6             | 0           | 0.210400 -1.693520 1.853001 |
| 35            | 6             | 0           | 1.106310 -1.330756 2.877698 |
| 36            | 6             | 0           | -0.815978 -2.604424 2.175638 |
| 37            | 6             | 0           | 1.004813 -1.877575 4.158458 |
| 38            | 1             | 0           | 1.880709 -0.601349 2.656948 |
| 39            | 6             | 0           | -0.934368 -3.140179 3.458421 |
| 40            | 1             | 0           | -1.527237 -2.890245 1.406169 |
| 41            | 6             | 0           | -0.017869 -2.783971 4.454866 |
| 42            | 1             | 0           | 1.713388 -1.584747 4.929653 |
|   |   |   |        |        |        |
|---|---|---|--------|--------|--------|
| 43 | 1 | 0 | -1.736171 | -3.840534 | 3.681811 |
| 44 | 1 | 0 | -0.104600 | -3.204840 | 5.453585 |
| 45 | 6 | 0 | -0.210085 | 1.693586 | 1.852973 |
| 46 | 6 | 0 | -1.105815 | 1.330869 | 2.877844 |
| 47 | 6 | 0 | 0.816358  | 2.604493 | 2.175394 |
| 48 | 6 | 0 | -1.004083 | 1.877732 | 4.158566 |
| 49 | 1 | 0 | -1.880261 | 0.601461 | 2.657261 |
| 50 | 6 | 0 | 0.934983  | 3.140293 | 3.458136 |
| 51 | 1 | 0 | 1.527481  | 2.890284 | 1.405788 |
| 52 | 6 | 0 | 0.018660  | 2.784129 | 4.454759 |
| 53 | 1 | 0 | -1.712523 | 1.584938 | 4.929897 |
| 54 | 1 | 0 | 1.736831  | 3.840649 | 3.681355 |
| 55 | 1 | 0 | 0.105574  | 3.205032 | 5.453446 |
| 56 | 17| 0 | 2.825624 | -0.069813 | -3.029943 |
| 57 | 8 | 0 | -3.428341 | 0.114431 | 0.204457 |
| 58 | 6 | 0 | -4.509526 | -0.858299 | 0.025378 |
| 59 | 6 | 0 | -3.988413 | 1.452084 | 0.393571 |
| 60 | 6 | 0 | -5.801517 | -0.039896 | -0.006058 |
| 61 | 1 | 0 | -4.322437 | -1.402280 | -0.903083 |
| 62 | 1 | 0 | -4.463745 | -1.543895 | 0.878305 |
| 63 | 6 | 0 | -5.435270 | 1.211642 | 0.810226 |
| 64 | 1 | 0 | -3.373125 | 1.956718 | 1.140721 |
| 65 | 1 | 0 | -3.928245 | 1.986320 | -0.562848 |
| 66 | 1 | 0 | -6.646421 | -0.594230 | 0.414087 |
| 67 | 1 | 0 | -6.048097 | 0.235302 | -1.037141 |
| 68 | 1 | 0 | -5.496570 | 1.009748 | 1.886463 |
| 69 | 1 | 0 | -6.074188 | 2.071119 | 0.585199 |
| 70 | 8 | 0 | 3.428340  | -0.114422 | 0.203916 |
| 71 | 6 | 0 | 3.988454  | -1.452066 | 0.392965 |
| 72 | 6 | 0 | 4.509488  | 0.858313 | 0.024646 |
| 73 | 6 | 0 | 5.435381  | -1.211609 | 0.809360 |
| 74 | 1 | 0 | 3.373300  | -1.956688 | 1.140232 |
| 75 | 1 | 0 | 3.928122  | -1.986322 | -0.563430 |
| 76 | 6 | 0 | 5.801475  | 0.039919 | -0.007007 |
| 77 | 1 | 0 | 4.322238  | 1.402290 | -0.903784 |
| 78 | 1 | 0 | 4.463850  | 1.543912 | 0.877576 |
| 79 | 1 | 0 | 6.074263  | -2.071086 | 0.584234 |
| 80 | 1 | 0 | 5.496870  | -1.009701 | 1.885581 |
| 81 | 1 | 0 | 6.047873  | -0.235292 | -1.038127 |
| 82 | 1 | 0 | 6.646447  | 0.594262 | 0.412979 |

**IM4**

298K, 1 atm, gas phase

Thermal correction to Enthalpy = 0.720152 Hartree

Thermal correction to Gibbs Free Energy = 0.582964 Hartree

Sum of electronic and thermal Enthalpies = -2912.077341 Hartree

S39
Sum of electronic and thermal Free Energies = -2912.214529 Hartree
298K, in THF
Sum of electronic and thermal Free Energies= -2912.247676 Hartree

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
|               |               | X           | Y           | Z           |
| 1             | 21            | 0           | 0.004603    | -1.784634   | -0.122078   |
| 2             | 17            | 0           | -0.097556   | -2.610996   | -2.499117   |
| 3             | 6             | 0           | -1.485444   | -0.375984   | -0.648449   |
| 4             | 6             | 0           | -0.740051   | 0.639857    | 0.094332    |
| 5             | 6             | 0           | 0.693747    | 0.668293    | 0.018114    |
| 6             | 6             | 0           | 1.398457    | -0.342107   | -0.773861   |
| 7             | 21            | 0           | -0.120894   | 0.099085    | -2.265740   |
| 8             | 14            | 0           | 3.222410    | -0.600755   | -1.066998   |
| 9             | 14            | 0           | -3.326388   | -0.571774   | -0.896911   |
| 10            | 6             | 0           | 4.304334    | -0.293461   | 0.472687    |
| 11            | 1             | 0           | 5.355468    | -0.509703   | 0.235683    |
| 12            | 1             | 0           | 4.247693    | 0.740713    | 0.828894    |
| 13            | 1             | 0           | 4.018064    | -0.947382   | 1.307783    |
| 14            | 6             | 0           | 3.920807    | 0.470956    | -2.476645   |
| 15            | 1             | 0           | 4.982985    | 0.245349    | -2.644644   |
| 16            | 1             | 0           | 3.393279    | 0.294322    | -3.423037   |
| 17            | 1             | 0           | 3.841427    | 1.541412    | -2.252562   |
| 18            | 6             | 0           | 3.504631    | -2.416963   | -1.564242   |
| 19            | 1             | 0           | 4.563285    | -2.580980   | -1.807357   |
| 20            | 1             | 0           | 3.250057    | -3.114509   | -0.752953   |
| 21            | 1             | 0           | 2.910088    | -2.703637   | -2.438798   |
| 22            | 6             | 0           | -4.285034   | 1.063110    | -1.021930   |
| 23            | 1             | 0           | -3.873359   | 1.704868    | -1.810989   |
| 24            | 1             | 0           | -5.334489   | 0.857364    | -1.275113   |
| 25            | 1             | 0           | -4.269874   | 1.635450    | -0.088174   |
| 26            | 6             | 0           | -3.637056   | -1.524734   | -2.511380   |
| 27            | 1             | 0           | -3.108873   | -2.484245   | -2.543677   |
| 28            | 1             | 0           | -4.711211   | -1.725858   | -2.623584   |
| 29            | 1             | 0           | -3.324956   | -0.950186   | -3.394004   |
| 30            | 6             | 0           | -4.123657   | -1.601805   | 0.503038    |
| 31            | 1             | 0           | -5.202543   | -1.724335   | 0.335260    |
| 32            | 1             | 0           | -3.687201   | -2.609465   | 0.556558    |
| 33            | 1             | 0           | -3.996390   | -1.122679   | 1.482260    |
| 34            | 6             | 0           | 1.456693    | 1.730996    | 0.755871    |
| 35            | 6             | 0           | 2.096455    | 2.760847    | 0.048127    |
| 36            | 6             | 0           | 1.580397    | 1.710374    | 2.153410    |
| 37            | 6             | 0           | 2.841191    | 3.736224    | 0.715641    |
38  1  0  1.998167   2.803171   -1.033842
39  6  0  2.330007   2.679379    2.107978
40  1  0  1.073609   0.933774    2.722212
41  6  0  2.966127   3.696704    2.107978
42  1  0  3.321302   4.528917    0.146952
43  1  0  2.411675   2.643650    3.909279
44  1  0  3.547443   4.453487    2.628440
45  6  0  -1.456213   1.676523    0.910978
46  6  0  -2.098264   1.323145    2.107700
47  6  0  -1.534734   3.010947    0.483819
48  6  0  -2.792954   2.271859    2.862304
49  1  0  -2.053248   0.290839    2.449313
50  6  0  -2.231685   3.962445    1.232365
51  1  0  -1.053530   3.302710   -0.448585
52  6  0  -2.863388   3.598315    2.425338
53  1  0  -3.281147   1.975553    3.788053
54  1  0  -2.283097   4.989682    0.879932
55  1  0  -3.406579   4.338788    3.006889
56 17  0  -0.211304   1.871526    -3.862582
57  8  0   0.166815  -2.701951    1.897188
58  6  0  -0.926024  -3.275449    2.692555
59  6  0   1.397171  -2.632784    2.699704
60  6  0  -0.249531  -3.845815    3.937151
61  1  0  -1.625510  -2.467668    2.929978
62  1  0  -1.429886  -4.022011    2.073577
63  6  0   0.944289  -2.896107    4.133115
64  1  0   2.076146  -3.407850    2.328686
65  1  0   1.842772  -1.648594    2.539037
66  1  0   0.097099  -4.869120    3.752285
67  1  0  -0.927912  -3.864804    4.795012
68  1  0   1.744175  -3.332889    4.738130
69  1  0   0.623141  -1.964207    4.612413

3a
298K, 1 atm, gas phase
Thermal correction to Enthalpy = 1.030420 Hartree
Thermal correction to Gibbs Free Energy = 0.851151 Hartree
Sum of electronic and thermal Enthalpies = -5359.859848 Hartree
Sum of electronic and thermal Free Energies = -5359.680578 Hartree

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
|               | 21            |             | X          Y          Z     |
| 1             | 21            | 0.000038767 | -0.000028525 | -0.000034431 |
|    |     |                  |                  |                  |                  |
|----|-----|------------------|------------------|------------------|------------------|
| 2  | 17  | -0.000006085     | -0.000001792     | 0.000001936      |                  |
| 3  | 6   | -0.000082477     | -0.000001339     | -0.000006665     |                  |
| 4  | 6   | 0.000079169      | -0.000006407     | 0.000027379      |                  |
| 5  | 6   | -0.000076497     | 0.000005640      | 0.000028565      |                  |
| 6  | 6   | 0.000082343      | 0.0000001735     | -0.000006602     |                  |
| 7  | 21  | -0.000039258     | 0.000028489      | -0.000035471     |                  |
| 8  | 14  | -0.000031794     | -0.000013573     | 0.000011797      |                  |
| 9  | 14  | 0.000031620      | 0.000013470      | 0.00011811       |                  |
| 10 | 6   | -0.000006480     | -0.000013487     | -0.000000052     |                  |
| 11 | 1   | 0.0000010427     | -0.000000642     | 0.000005545      |                  |
| 12 | 1   | -0.000002535     | 0.000010969      | -0.000005763     |                  |
| 13 | 1   | 0.000001840      | -0.000001817     | -0.000003964     |                  |
| 14 | 6   | -0.000004164     | -0.000002181     | 0.000004770      |                  |
| 15 | 1   | 0.000001568      | -0.000001089     | 0.000001599      |                  |
| 16 | 1   | 0.000001636      | -0.000002409     | -0.000003618     |                  |
| 17 | 1   | -0.000000663     | 0.000003577      | -0.000000132     |                  |
| 18 | 6   | -0.000006259     | 0.000020250      | -0.00017539      |                  |
| 19 | 1   | -0.000000448     | -0.000002245     | 0.000005383      |                  |
| 20 | 1   | -0.000000963     | 0.000001312      | 0.000000421      |                  |
| 21 | 1   | 0.000002619      | 0.000000167      | 0.000000821      |                  |
| 22 | 6   | 0.000006180      | -0.000002049     | -0.000017425     |                  |
| 23 | 1   | -0.000002579     | -0.000000244     | 0.00000817       |                  |
| 24 | 1   | 0.000000397      | 0.000002184      | 0.000005292      |                  |
| 25 | 1   | 0.000000961      | -0.000001542     | 0.000000935      |                  |
| 26 | 6   | 0.0000004031     | 0.000002227      | 0.000004766      |                  |
| 27 | 1   | 0.000000082      | -0.000003598     | -0.00000196      |                  |
| 28 | 1   | -0.000001497     | 0.000001073      | 0.000001717      |                  |
| 29 | 1   | -0.000001625     | 0.000002387      | -0.000003624     |                  |
| 30 | 6   | 0.000006645      | 0.000013415      | 0.00000081      |                  |
| 31 | 1   | -0.000001387     | 0.000000647      | 0.000005569      |                  |
| 32 | 1   | 0.000002481      | -0.000010948     | -0.000005793     |                  |
| 33 | 1   | -0.000001820     | 0.000001844      | -0.000003918     |                  |
| 34 | 6   | 0.000068420      | 0.00001721       | -0.000004743     |                  |
| 35 | 6   | 0.000001281      | 0.000011800      | -0.000021438     |                  |
| 36 | 6   | 0.000009154      | 0.000016377      | -0.000032669     |                  |
| 37 | 6   | -0.000000458     | 0.000003544      | -0.000001007     |                  |
| 38 | 1   | -0.000001527     | -0.000004907     | 0.000004525      |                  |
| 39 | 6   | 0.000003390      | -0.00000432      | 0.000014872      |                  |
| 40 | 1   | -0.000004893     | 0.000002372      | -0.00001653      |                  |
| 41 | 6   | -0.000007986     | -0.000004505     | -0.000004850     |                  |
| 42 | 1   | -0.000000815     | -0.00000938      | 0.000001325      |                  |
| 43 | 1   | -0.000000498     | 0.000002026      | -0.00000641      |                  |
| 44 | 1   | 0.000001972      | -0.00000696      | 0.00000164       |                  |
| 45 | 6   | -0.000070477     | 0.000000559      | -0.000007961     |                  |
| 46 | 6   | -0.000001177     | -0.000012220     | -0.000020986     |                  |
| 47 | 6   | -0.000010034     | -0.000016640     | -0.000032729     |                  |
|   |   |       |       |       |       |
|---|---|-------|-------|-------|-------|
|   |   | 48.0000000679 | -0.000003973 | -0.000000913 |   |
|   | 6 | 0.0000001645 | 0.0000004164 | 0.0000004335 |   |
|   | 6 | -0.0000003195 | 0.0000000230 | 0.0000015553 |   |
|   | 1 | 0.0000005413 | -0.000002115 | -0.000002205 |   |
|   | 6 | 0.0000007945 | 0.0000005210 | -0.000005421 |   |
|   | 1 | 0.0000000833 | 0.0000000871 | 0.000001398 |   |
|   | 1 | 0.0000000502 | -0.000002001 | -0.000000725 |   |
|   | 6 | -0.000001978 | 0.000000644 | 0.000000153 |   |
|   | 17 | 0.000006240 | 0.000001775 | 0.000002093 |   |
|   | 8 | -0.0000003494 | -0.0000001622 | 0.0000116352 |   |
|   | 6 | 0.0000038711 | -0.000005542 | -0.000028557 |   |
|   | 6 | -0.000007816 | 0.0000046424 | -0.000021174 |   |
|   | 6 | -0.0000019320 | 0.000007884 | -0.000009506 |   |
|   | 1 | -0.0000005334 | -0.000003249 | 0.000001155 |   |
|   | 6 | -0.000000750 | -0.000001057 | 0.000004635 |   |
|   | 6 | 0.0000009410 | -0.000008260 | -0.000004393 |   |
|   | 1 | 0.000002687 | -0.000008103 | -0.000001742 |   |
|   | 1 | 0.000002752 | 0.000003765 | 0.000003427 |   |
|   | 6 | 0.000001525 | 0.000001125 | 0.000002339 |   |
|   | 6 | 0.000002533 | -0.000002522 | -0.000001239 |   |
|   | 6 | 0.000002664 | 0.000000088 | 0.000000704 |   |
|   | 1 | -0.000000196 | 0.000000728 | -0.000000853 |   |
|   | 8 | 0.0000004352 | 0.000001915 | 0.000116703 |   |
|   | 6 | 0.000007475 | -0.0000047405 | -0.000020883 |   |
|   | 6 | -0.0000039295 | 0.000006199 | -0.000029536 |   |
|   | 6 | -0.0000010108 | 0.000007796 | -0.000004515 |   |
|   | 6 | -0.000002484 | 0.000007744 | -0.000001434 |   |
|   | 1 | -0.000002228 | -0.000003858 | 0.000003546 |   |
|   | 6 | 0.0000019307 | -0.000007681 | -0.000009454 |   |
|   | 1 | 0.0000005652 | 0.000003863 | 0.000001241 |   |
|   | 1 | 0.0000001090 | 0.000001152 | 0.000004577 |   |
|   | 1 | 0.0000000666 | -0.000000892 | -0.000000880 |   |
|   | 1 | -0.0000003079 | -0.000000360 | 0.000000617 |   |
|   | 1 | -0.000002718 | 0.000002870 | -0.000001231 |   |
|   | 1 | -0.000001671 | -0.000000922 | 0.000002314 |   |

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