Supplementary Information (SI) for ChemComm.
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In Crystallo Homolytic Cleavage of a Terminal Lanthanum(III)- Methyl Bond by Cu Kα X-Radiation Forms a La(II) Complex

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Supporting Information

The Supporting Information contains:

1. Experimental.

General Considerations. All manipulations were performed by using modified Schlenk techniques or in a Vacuum/Atmospheres glovebox under argon. Solvents were degassed by sparging with dry argon before drying and collection using a Grubbs-type[1] solvent purification system (JC Meyer). The methyl complex $Ln(SAr^{iPr6})_2CH_3$, **1**, was prepared by treatment of $Ln(SAr^{iPr6})_2I$[2] with methyllithium in diethyl ether as previously described.[3] Crystals of **1** were covered in Paratone oil in an argon-filled glovebox. A suitable crystal was then selected and mounted in a nylon cryoloop and immediately transferred to the nitrogen cold stream of the diffractometer. Data were collected on samples cooled to 100 K using a dual source Bruker D8 Venture diffractometer equipped with a Bruker PHOTON III CMOS detector. For this study, Cu Kα radiation (Bruker IμS DIAMOND-II, 50 W, λ = 1.54 Å) was used to study the transformation of $Ln(SAr^{iPr6})_2CH_3$, **1**, to $La(SAr^{iPr6})_2$,[2, 4] **2**, by radiolysis.

2. Crystallographic Details

Table S1. X-ray data collection parameters and crystallographic details for La(SAr^{iPr6})$_2$CH$_3$·0.5(C_6H_{14}), **1 · 0.5(C_6H_{14})**, after experiment 1 (5 Hours of X-ray Irradiation).

Note: Fractional values for C and H are given in the following formula due to the partial occupancy of the methyl carbon bound to lanthanum that results from the formation of La(SAr^{iPr6})$_2$, **2**, under the conditions of the diffraction experiment.

Empirical formula	$LaS_2C_{75.87}H_{107.61}$
Formula weight	1222.69
Temperature/K	101.00
Crystal system	monoclinic
Space group	C2/c
a/Å	21.1776(11)
b/Å	18.2359(10)
c/Å	36.0813(19)
α/°	90
β/°	91.179(2)
γ/°	90
Volume/Å^3	13931.4(13)
Z	8
ρ_{calc}g/cm^3	1.166
μ/mm^{-1}	5.578
F(000)	5215.0
Crystal size/mm^3	0.155 × 0.151 × 0.138
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.9 to 155.186
Index ranges	-26 ≤ h ≤ 25, -23 ≤ k ≤ 23, -45 ≤ l ≤ 45
Reflections collected	125351
Independent reflections	14771 [R_{int} = 0.0602, R_{sigma} = 0.0317]
Data/restraints/parameters	14771/0/793
Goodness-of-fit on F^2	1.178
Final R indexes [I>=2σ (I)]	R_1 = 0.0444, wR_2 = 0.1064
Final R indexes [all data]	R_1 = 0.0448, wR_2 = 0.1066
Largest diff. peak/hole / e Å^{-3}	0.54/-0.64

X-ray Data Collection, Structure Solution and Refinement for La(SAr^{iPr6})$_2CH_3$·0.5(C_6H_{14}), 1 · 0.5(C_6H_{14}) After Experiment 1 (5 h of X-ray Irradiation).

A yellow crystal of approximate dimensions 0.138 x 0.151 x 0.155 mm was mounted in a cryoloop and transferred to a Bruker D8 Venture diffractometer system. The APEX5[5] program package was used to determine the unit-cell parameters and for data collection (1-5 sec/frame scan time). The raw frame data was processed using SAINT[6] and SADABS[7] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[8] program package. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space groups *Cc* and *C*2/*c*. It was later determined that space group C2/c was correct.

The structure was solved by direct methods and refined on F2 by full-matrix least-squares techniques. The analytical scattering factors[9] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The occupancies of the La, La1, and C1 atoms were first refined freely until a stable model was obtained and then the occupancies of the La1 and C1 atoms were fixed to the occupancy of the freely refined C1 atom and rounded to the nearest hundredth (0.87). The occupancy of La1A was then fixed to the remaining balance (0.13). The disordered C21 atom (isopropyl group) was included using two components with partial site occupancy factors. Least-squares analysis yielded wR_2 = 0.1066 and Goof = 1.178 for 793 variables refined against 14771 data (0.79 Å), R1 = 0.0444 for those 14605 data with I > 2.0σ(I).

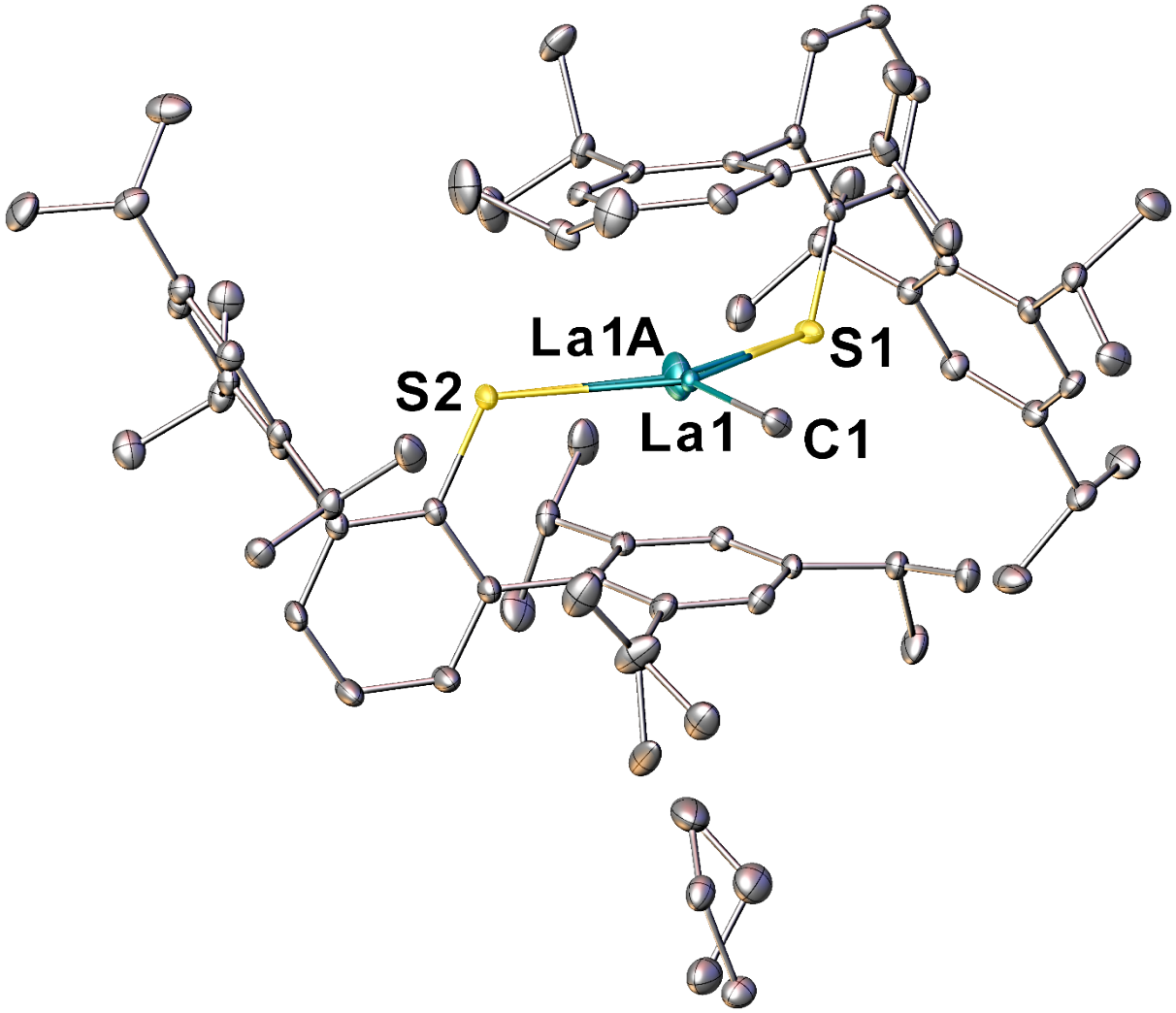

Figure S1. The molecular structure of La(SAr^{iPr6})$_2$CH$_3$,**1**, showing the conversion of **1** to **2** after a 5 h data collection using Cu Kα X-rays. Hydrogen atoms are not shown. The occupancies of La1 and C1 are 87%, while the occupancy of La1A is 13%.

Table S2. X-ray data collection parameters and crystallographic details for La(SAr^{iPr6})$_2$CH$_3$·0.5(C_6H_{14}), **1 · 0.5(C_6H_{14})**, after experiment 2 (10 Hours of X-ray Irradiation).

Note: Fractional values for C and H are given in the following formula due to the partial occupancy of the methyl carbon bound to lanthanum that results from the formation of La(SAr^{iPr6})$_2$, **2**, under the conditions of the diffraction experiment.

Empirical formula	$C_{75.73}H_{107.19}LaS_2$
Formula weight	1220.59
Temperature/K	100.00
Crystal system	monoclinic
Space group	C2/c
a/Å	21.1388(8)
b/Å	18.2563(6)
c/Å	36.1180(13)
α/°	90
β/°	91.482(2)
γ/°	90
Volume/Å^3	13933.9(9)
Z	8
ρ_{calc}g/cm^3	1.164
μ/mm^{-1}	5.576
F(000)	5205.0
Crystal size/mm^3	0.155 × 0.151 × 0.138
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.894 to 155.342
Index ranges	-26 ≤ h ≤ 25, -23 ≤ k ≤ 23, -45 ≤ l ≤ 45
Reflections collected	144834
Independent reflections	14796 [R_{int} = 0.0636, R_{sigma} = 0.0295]
Data/restraints/parameters	14796/84/840
Goodness-of-fit on F^2	1.197
Final R indexes [I>=2σ (I)]	R_1 = 0.0524, wR_2 = 0.1284
Final R indexes [all data]	R_1 = 0.0529, wR_2 = 0.1286
Largest diff. peak/hole / e Å^{-3}	0.78/-0.72

X-ray Data Collection, Structure Solution and Refinement for La(SAr^{iPr6})$_2CH_3$·0.5(C_6H_{14}), 1 · 0.5(C_6H_{14}) After Experiment 2 (10 h of X-ray Irradiation).

Without disturbing the crystal from Experiment 1, the identical data collection strategy was executed a second time. As described above, the APEX5[5] program package was used to determine the unit-cell parameters and for data collection (1-5 sec/frame scan time). The raw frame data was processed using SAINT[6] and SADABS[7] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[8] program package. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space groups *Cc* and *C*2/*c*. It was later determined that space group C2/c was correct.

The structure was solved by direct methods and refined on F2 by full-matrix least-squares techniques. The analytical scattering factors[9] for neutral atoms were used throughout the analysis. The occupancies of the La, La1, and C1 atoms were first refined freely until a stable model was obtained and then the occupancies of the La1 and C1 atoms were fixed to the occupancy of the freely refined C1 atom and rounded to the nearest hundredth (0.73). The occupancy of La1A was then fixed to the remaining balance (0.27). Further disorder related to the conversion of **1** to **2** was modeled using the same ratio of occupancies. Least-squares analysis yielded wR_2 = 0.1286 and Goof = 1.197 for 840 variables refined against 14796 data (0.79 Å), R1 = 0.0524 for those 14518 data with I > 2.0σ(I).

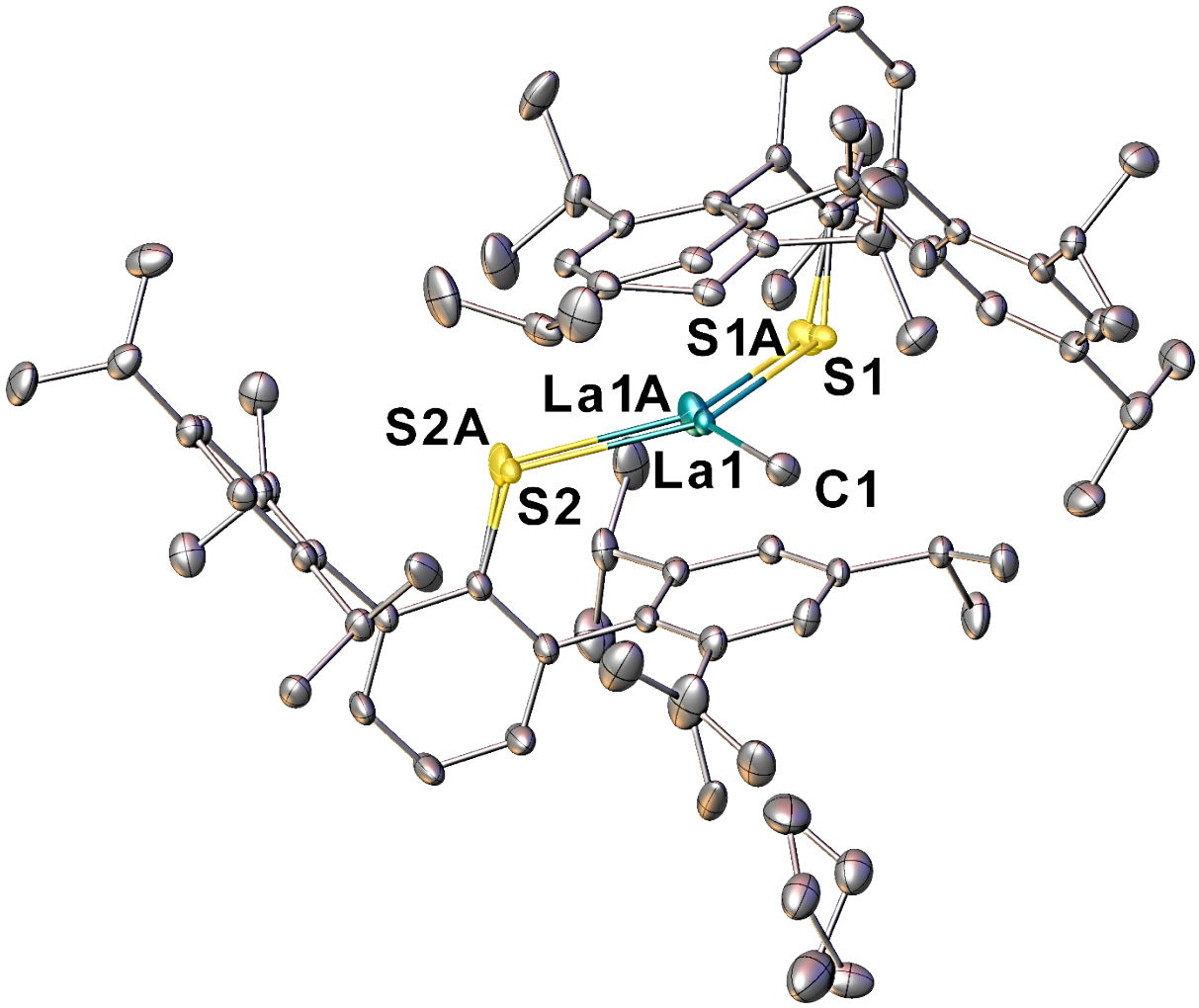

Figure S2. The molecular structure of La(SAr^{iPr6})$_2$CH$_3$,**1**, showing the conversion of **1** to **2** after 10 h of data collection using Cu Kα X-rays. Hydrogen atoms are not shown. The occupancies of La1, C1, S1, and S2 are 78%, while the occupancies of La1A, S1A, and S2A are 22%. The occupancies of the affected carbons of the disordered flanking ring have been fixed to the same ratio in the model.

Table S3. X-ray data collection parameters and crystallographic details for $La(SAr^{iPr6})_2CH_3 \cdot 0.5(C_6H_{14})$, **$1 \cdot 0.5(C_6H_{14})$**, after Experiment 3 (15 Hours of X-ray Irradiation).

Note: Fractional values for C and H are given in the following formula due to the partial occupancy of the methyl carbon bound to lanthanum that results from the formation of $La(SAr^{iPr6})_2$, **2**, under the conditions of the diffraction experiment.

Empirical formula	$LaS_2C_{75.63}H_{106.89}$
Formula weight	1219.08
Temperature/K	100.00
Crystal system	monoclinic
Space group	C2/c
a/Å	21.1136(7)
b/Å	18.2758(6)
c/Å	36.1580(13)
α/°	90
β/°	91.790(2)
γ/°	90
Volume/Å^3	13945.4(8)
Z	8
ρ_{calc}g/cm^3	1.161
μ/mm^{-1}	5.571
F(000)	5197.0
Crystal size/mm^3	0.155 × 0.151 × 0.138
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.89 to 155.044
Index ranges	-26 ≤ h ≤ 25, -23 ≤ k ≤ 23, -45 ≤ l ≤ 45
Reflections collected	142504
Independent reflections	14804 [R_{int} = 0.0652, R_{sigma} = 0.0318]
Data/restraints/parameters	14804/189/908
Goodness-of-fit on F^2	1.225
Final R indexes [I>=2σ (I)]	R_1 = 0.0592, wR_2 = 0.1383
Final R indexes [all data]	R_1 = 0.0605, wR_2 = 0.1389
Largest diff. peak/hole / e Å^{-3}	0.46/-0.72

X-ray Data Collection, Structure Solution and Refinement for La(SAr^{iPr6})$_2$CH$_3$·0.5(C$_6$H$_{14}$), 1 · (C$_6$H$_{14}$) After Experiment 3 (15 h of X-ray Irradiation).

Without disturbing the crystal from Experiments 1 and 2, the identical data collection strategy was executed a third time. As described above, the APEX5[5] program package was used to determine the unit-cell parameters and for data collection (1-5 sec/frame scan time). The raw frame data was processed using SAINT[6] and SADABS[7] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[8] program package. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space groups *Cc* and *C*2/*c*. It was later determined that space group C2/c was correct.

The structure was solved by direct methods and refined on F2 by full-matrix least-squares techniques. The analytical scattering factors[9] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The occupancies of the La, La1, and C1 atoms were first refined freely until a stable model was obtained and then the occupancies of the La1 and C1 atoms were fixed to the occupancy of the freely refined C1 atom and rounded to the nearest hundredth (0.63). The occupancy of La1A was then fixed to the remaining balance (0.37). Further disorder related to the conversion of **1** to **2** was modeled using the same ratio of occupancies. Least-squares analysis yielded wR_2 = 0.1389 and Goof = 1.225 for 908 variables refined against 14804 data (0.79 Å), R1 = 0.0592 for those 14308 data with I > 2.0σ(I).

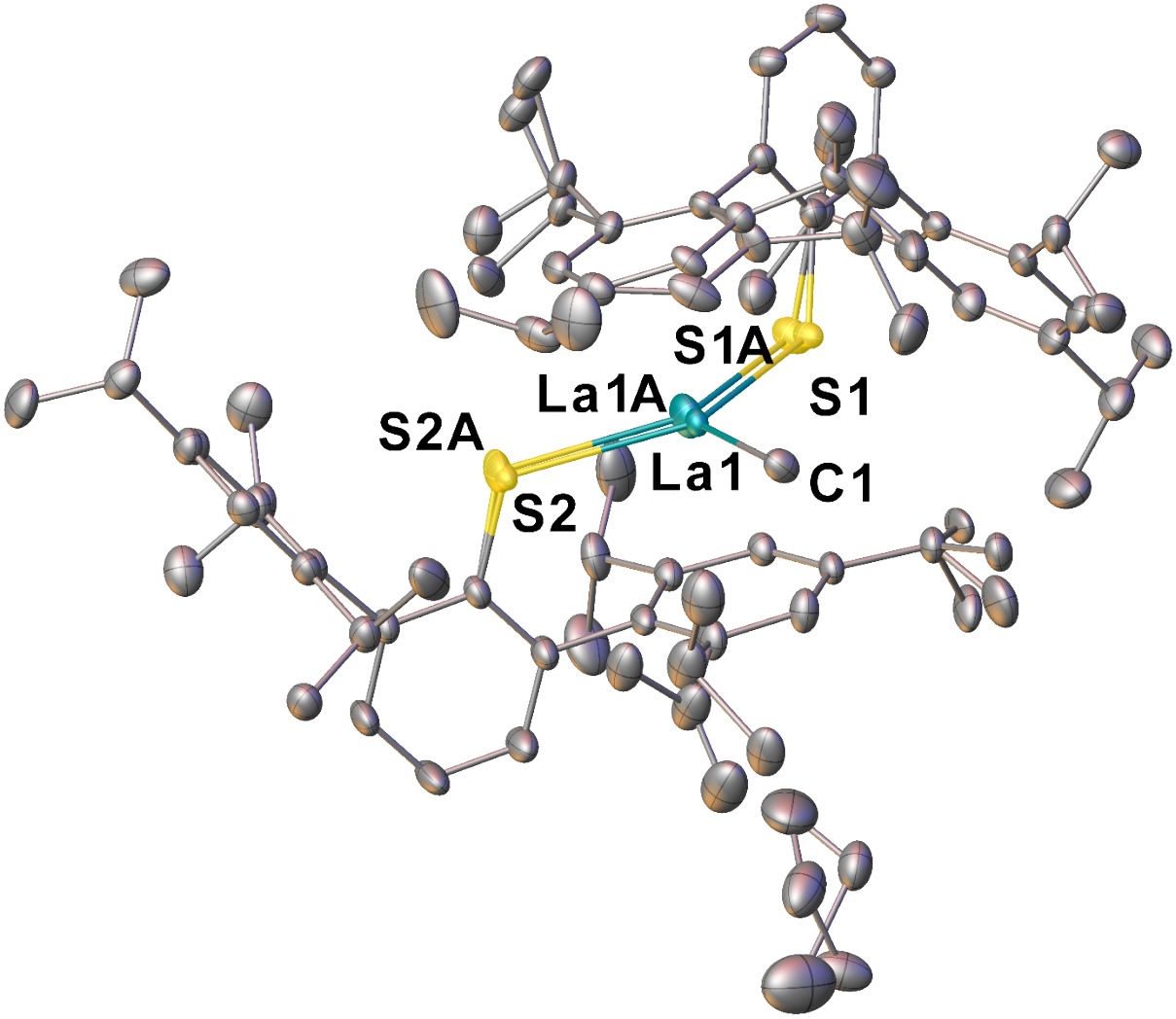

Figure S3. The molecular structure of La(SAr^{iPr6})$_2$CH$_3$,**1**, showing the conversion of **1** to **2** after 15 h of data collection using Cu Kα X-rays. Hydrogen atoms are not shown. The occupancies of La1, C1, S1, and S2 are 65%, while the occupancies of La1A, S1A, and S2A are 35%. The occupancies of the affected carbons of the disordered flanking ring have been fixed to the same ratio in the model.

Table S4. X-ray data collection parameters and crystallographic details for $La(SAr^{iPr6})_2CH_3 \cdot 0.5(C_6H_{14})$, **$1 \cdot 0.5(C_6H_{14})$**, after Experiment 4 (20 Hours of X-ray Irradiation).

Note: Fractional values for C and H are given in the following formula due to the partial occupancy of the methyl carbon bound to lanthanum that results from the formation of $La(SAr^{iPr6})_2$, **2**, under the conditions of the diffraction experiment.

Empirical formula	$LaS_2C_{75.53}H_{106.59}$
Formula weight	1217.58
Temperature/K	100.00
Crystal system	monoclinic
Space group	C2/c
a/Å	21.0895(8)
b/Å	18.2926(6)
c/Å	36.1914(16)
α/°	90
β/°	92.017(2)
γ/°	90
Volume/Å^3	13953.3(9)
Z	8
ρ_{calc}g/cm^3	1.159
μ/mm^{-1}	5.567
F(000)	5190.0
Crystal size/mm^3	0.155 × 0.151 × 0.138
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.886 to 155.508
Index ranges	-26 ≤ h ≤ 25, -23 ≤ k ≤ 23, -45 ≤ l ≤ 45
Reflections collected	139288
Independent reflections	14812 [R_{int} = 0.0686, R_{sigma} = 0.0348]
Data/restraints/parameters	14812/210/918
Goodness-of-fit on F^2	1.201
Final R indexes [I>=2σ (I)]	R_1 = 0.0699, wR_2 = 0.1628
Final R indexes [all data]	R_1 = 0.0720, wR_2 = 0.1637
Largest diff. peak/hole / e Å^{-3}	0.53/-0.72

X-ray Data Collection, Structure Solution and Refinement for La(SAr^{iPr6})$_2$CH$_3$·0.5(C$_6$H$_{14}$), 1 · 0.5(C$_6$H$_{14}$) After Experiment 4 (20 h of X-ray Irradiation).

Without disturbing the crystal from Experiments 1-3, the identical data collection strategy was executed a fourth time. As described above, the APEX5[5] program package was used to determine the unit-cell parameters and for data collection (1-5 sec/frame scan time). The raw frame data was processed using SAINT[6] and SADABS[7] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[8] program package. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space groups *Cc* and *C*2/*c*. It was later determined that space group C2/c was correct.

The structure was solved by direct methods and refined on F2 by full-matrix least-squares techniques. The analytical scattering factors[9] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The occupancies of the La, La1, and C1 atoms were first refined freely until a stable model was obtained and then the occupancies of the La1 and C1 atoms were fixed to the occupancy of the freely refined C1 atom and rounded to the nearest hundredth (0.53). The occupancy of La1A was then fixed to the remaining balance (0.47). Further disorder related to the conversion of **1** to **2** was modeled using the same ratio of occupancies. Least-squares analysis yielded wR_2 = 0.1637 and Goof = 1.201 for 918 variables refined against 14812 data (0.79 Å), R1 = 0.0699 for those 14059 data with I > 2.0σ(I).

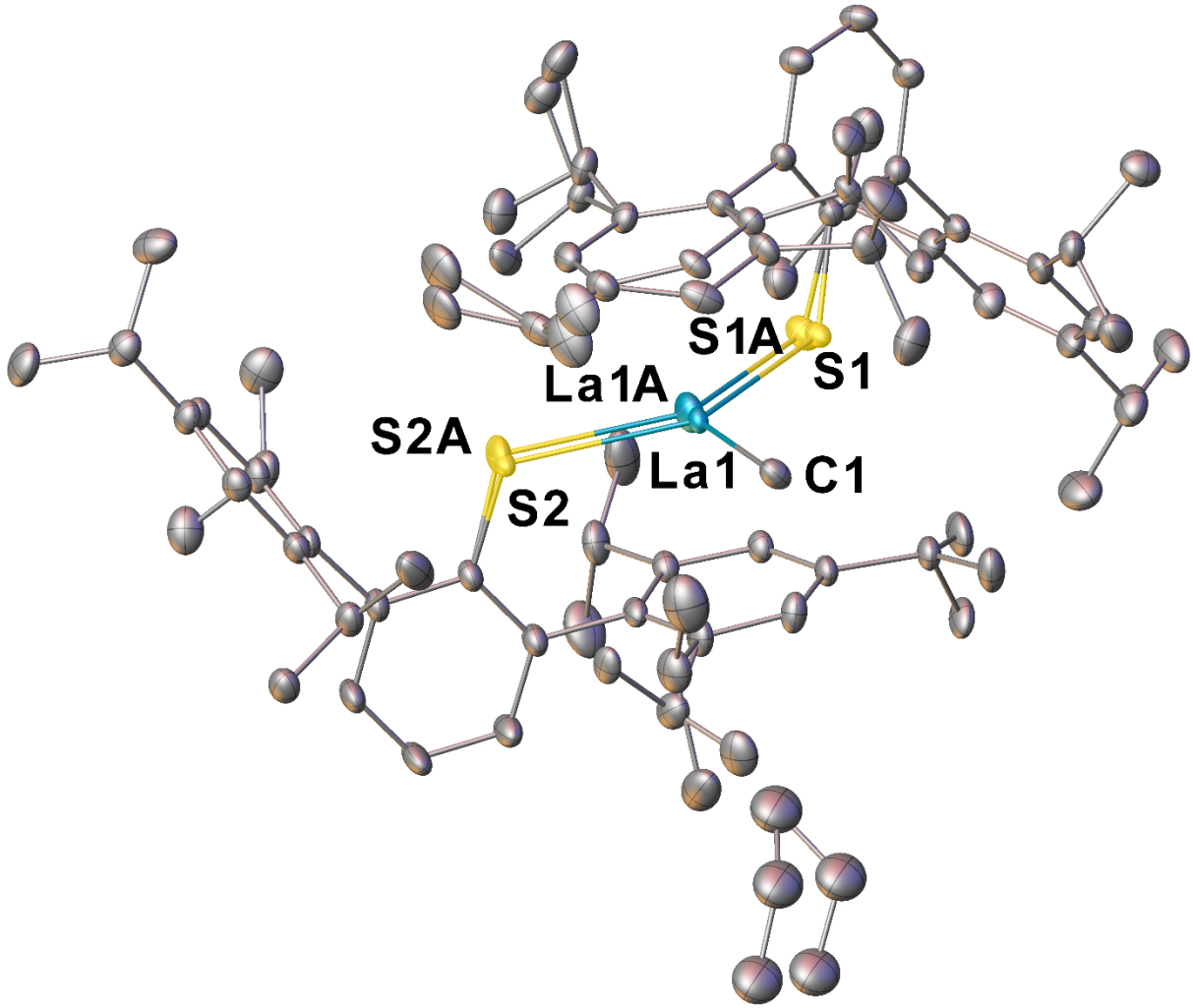

Figure S4. The molecular structure of La(SAr^{iPr6})$_2$CH$_3$,**1**, showing the conversion of **1** to **2** after 20 h of data collection using Cu Kα X-rays. Hydrogen atoms are not shown. The occupancies of La1, C1, S1, and S2 are 53%, while the occupancies of La1A, S1A, and S2A are 47%. The occupancies of the affected carbons of the disordered flanking ring have been fixed to the same ratio in the model.

Table S5. X-ray data collection parameters and crystallographic details for a second crystal of La(SAr^{iPr6})$_2$CH$_3$·0.5(C_6H_{14}), **1 · 0.5(C_6H_{14})**. These data were collected using Mo Kα X-rays.

Empirical formula	$C_{76}H_{108}LaS_2$
Formula weight	1224.65
Temperature/K	100.00
Crystal system	monoclinic
Space group	C2/c
a/Å	21.1869(7)
b/Å	18.2236(6)
c/Å	36.0444(15)
α/°	90
β/°	91.0380(10)
γ/°	90
Volume/Å^3	13914.5(9)
Z	8
ρ_{calc}g/cm^3	1.169
μ/mm^{-1}	0.713
F(000)	5224.0
Crystal size/mm^3	0.122 × 0.088 × 0.081
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.694 to 66.35
Index ranges	-32 ≤ h ≤ 24, -27 ≤ k ≤ 28, -55 ≤ l ≤ 55
Reflections collected	167876
Independent reflections	26556 [R_{int} = 0.0785, R_{sigma} = 0.0554]
Data/restraints/parameters	26556/0/766
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0387, wR_2 = 0.0816
Final R indexes [all data]	R_1 = 0.0611, wR_2 = 0.0910
Largest diff. peak/hole / e Å^{-3}	0.88/-0.41

X-ray Data Collection, Structure Solution and Refinement for a Second Crystal of $La(SAr^{iPr6})_2CH_3 \cdot 0.5(C_6H_{14})$, $1 \cdot 0.5(C_6H_{14})$ Using Mo Kα X-rays.

As described above, the APEX5[5] program package was used to determine the unit-cell parameters and for data collection (5 sec/frame scan time). The raw frame data was processed using SAINT[6] and SADABS[7] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[8] program package. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space groups *Cc* and *C*2/*c*. It was later determined that space group C2/c was correct.

The structure was solved by direct methods and refined on F2 by full-matrix least-squares techniques. The analytical scattering factors[9] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Least-squares analysis yielded $wR_2 = 0.0910$ and Goof = 1.027 for 766 variables refined against 26556 data (0.65 Å), R1 = 0.0387 for those 20217 data with $I > 2.0\sigma(I)$.

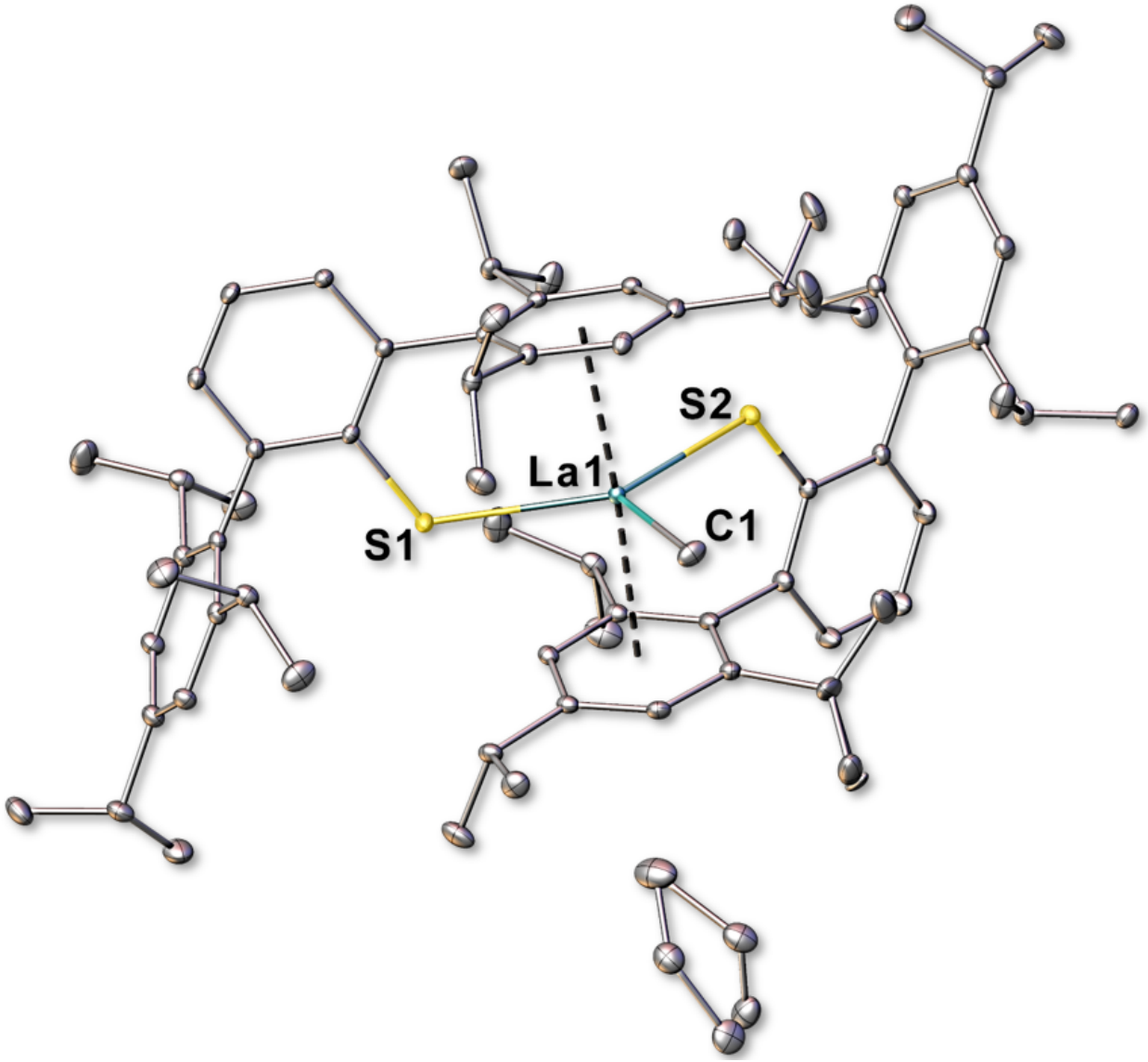

Figure S5. The molecular structure of a second crystal of La(SAr^{iPr6})$_2$CH$_3$, **1**, determined using Mo Kα X-rays. Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms are not shown.

Table S6. X-ray data collection parameters and crystallographic details for a second crystal of La(SAr^{iPr6})$_2$CH$_3$·0.5(C_6H_{14}), **1 · 0.5(C_6H_{14})**. These data were collected using Cu Kα X-rays over a period of 5h and 12 min.

Note: Fractional values for C and H are given in the following formula due to the partial occupancy of the methyl carbon bound to lanthanum that results from the formation of La(SAr^{iPr6})$_2$, **2**, under the conditions of the diffraction experiment.

Empirical formula	$LaS_2C_{75.93}H_{107.71}$
Formula weight	1223.51
Temperature/K	100.00
Crystal system	monoclinic
Space group	C2/c
a/Å	21.1898(4)
b/Å	18.2528(3)
c/Å	36.0951(7)
α/°	90
β/°	91.1970(10)
γ/°	90
Volume/Å^3	13957.6(4)
Z	8
ρ_{calc}g/cm^3	1.164
μ/mm^{-1}	5.568
F(000)	5218.0
Crystal size/mm^3	0.121 × 0.088 × 0.081
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.814 to 158.25
Index ranges	-24 ≤ h ≤ 26, -22 ≤ k ≤ 21, -45 ≤ l ≤ 45
Reflections collected	106690
Independent reflections	14790 [R_{int} = 0.0592, R_{sigma} = 0.0335]
Data/restraints/parameters	14790/96/840
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0321, wR_2 = 0.0764
Final R indexes [all data]	R_1 = 0.0354, wR_2 = 0.0779
Largest diff. peak/hole / e Å^{-3}	0.51/-0.42

X-ray Data Collection, Structure Solution and Refinement for a Second Crystal of La(SAr^{iPr6})$_2$CH$_3$·0.5(C$_6$H$_{14}$), 1 · 0.5(C$_6$H$_{14}$) (5 h and 12 min of X-ray Irradiation with Cu Kα X-rays).

Without disturbing the crystal from the experiment using Mo Kα radiation, data were collected again on this crystal using Cu Kα X-rays. As described above, the APEX5[5] program package was used to determine the unit-cell parameters and for data collection (4.5 sec/frame scan time). The raw frame data was processed using SAINT[6] and SADABS[7] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[8] program package. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space groups *Cc* and *C*2/*c*. It was later determined that space group C2/c was correct.

The structure was solved by direct methods and refined on F2 by full-matrix least-squares techniques. The analytical scattering factors[9] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The occupancies of the La, La1, and C1 atoms were first refined freely until a stable model was obtained and then the occupancies of the La1 and C1 atoms were fixed to the occupancy of the freely refined C1 atom and rounded to the nearest hundredth (0.93). The occupancy of La1A was then fixed to the remaining balance (0.07). Further disorder related to the conversion of **1** to **2** was modeled using the same ratio of occupancies. Least-squares analysis yielded wR_2 = 0.0779 and Goof = 1.031 for 840 variables refined against 14790 data (0.79 Å), R1 = 0.0321 for those 13657 data with I > 2.0σ(I).

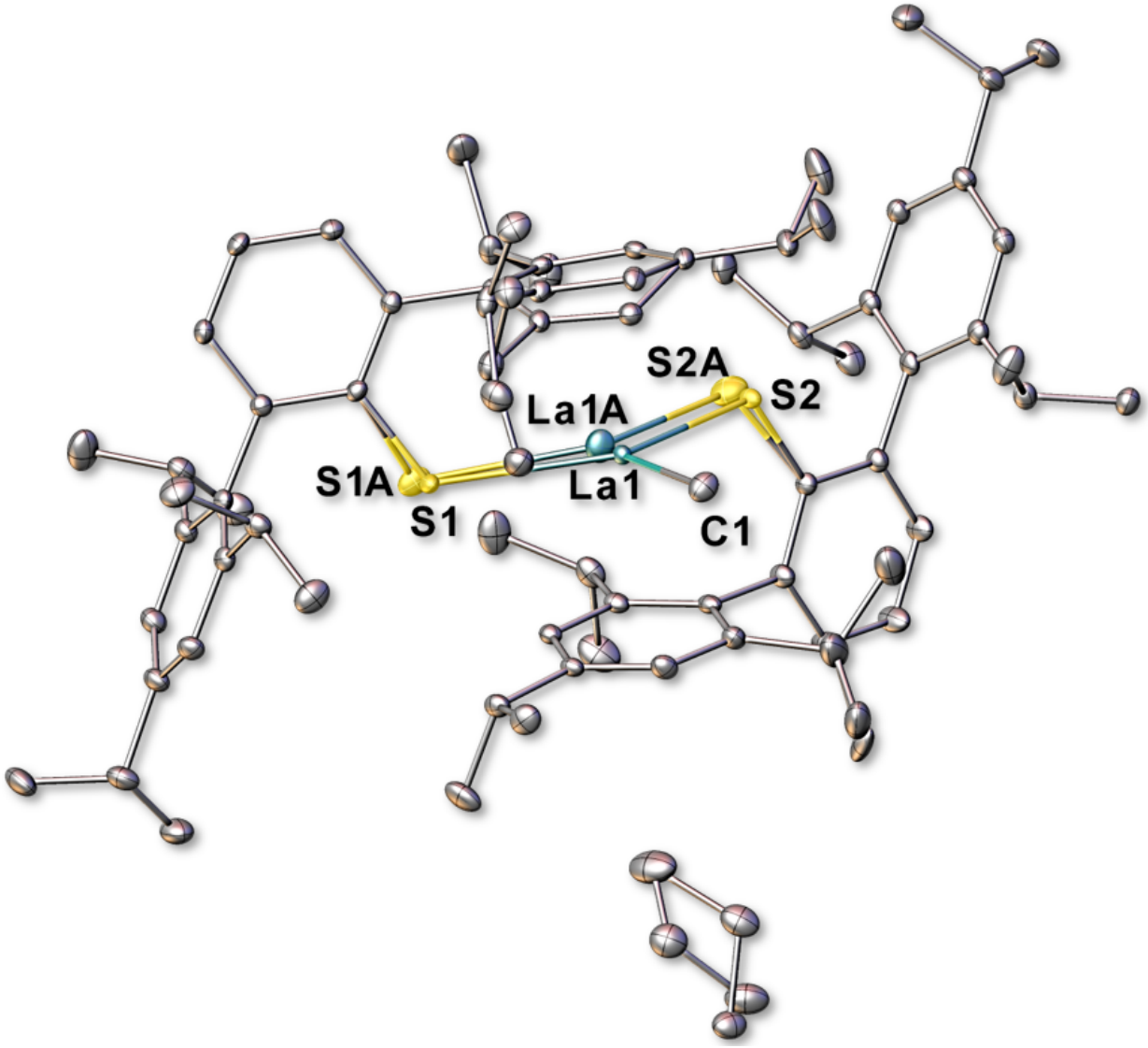

Figure S6. The molecular structure of a second crystal of La(SAr^{iPr6})$_2$CH$_3$, **1**, showing the conversion of **1** to **2** after 5 h and 12 min of data collection using Cu Kα X-rays. Hydrogen atoms are not shown. The occupancies of La1, C1, S1, and S2 are 93%, while the occupancies of La1A, S1A, and S2A are 7%. The occupancies of the affected carbons of the disordered flanking ring have been fixed to the same ratio in the model.

Table S7. X-ray data collection parameters and crystallographic details for a second crystal of La(SAr^{iPr6})$_2$CH$_3$·0.5(C_6H_{14}), **1 · 0.5(C_6H_{14})**. These data were collected using Cu Kα X-rays over a period of 5h and 12 min (total exposure to Cu Kα rays of 10h and 24 min).

Note: Fractional values for C and H are given in the following formula due to the partial occupancy of the methyl carbon bound to lanthanum that results from the formation of La(SAr^{iPr6})$_2$, **2**, under the conditions of the diffraction experiment.

Empirical formula	$LaS_2C_{75.77}H_{107.31}$
Formula weight	1221.19
Temperature/K	100.00
Crystal system	monoclinic
Space group	C2/c
a/Å	21.1612(5)
b/Å	18.2768(4)
c/Å	36.1515(9)
α/°	90
β/°	91.637(2)
γ/°	90
Volume/Å^3	13976.2(6)
Z	8
ρ_{calc}g/cm^3	1.161
μ/mm^{-1}	5.559
F(000)	5207.0
Crystal size/mm^3	0.115 × 0.097 × 0.082
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.8 to 157.546
Index ranges	-24 ≤ h ≤ 26, -22 ≤ k ≤ 21, -45 ≤ l ≤ 45
Reflections collected	109125
Independent reflections	14822 [R_{int} = 0.0647, R_{sigma} = 0.0362]
Data/restraints/parameters	14822/180/870
Goodness-of-fit on F^2	1.070
Final R indexes [I>=2σ (I)]	R_1 = 0.0439, wR_2 = 0.1061
Final R indexes [all data]	R_1 = 0.0504, wR_2 = 0.1095
Largest diff. peak/hole / e Å^{-3}	0.80/-0.55

X-ray Data Collection, Structure Solution and Refinement for a Second Crystal of La(SAr^{iPr6})$_2$CH$_3$·0.5(C_6H_{14}), 1 · 0.5(C_6H_{14}) (10 h and 24 min of X-ray Irradiation with Cu Kα X-rays).

Without disturbing the crystal from the prior experiment, data were collected again on this crystal using Cu Kα X-rays. As described above, the APEX5[5] program package was used to determine the unit-cell parameters and for data collection (4.5 sec/frame scan time). The raw frame data was processed using SAINT[6] and SADABS[7] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[8] program package. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space groups *Cc* and *C*2/*c*. It was later determined that space group C2/c was correct.

The structure was solved by direct methods and refined on F2 by full-matrix least-squares techniques. The analytical scattering factors[9] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The occupancies of the La, La1, and C1 atoms were first refined freely until a stable model was obtained and then the occupancies of the La1 and C1 atoms were fixed to the occupancy of the freely refined C1 atom and rounded to the nearest hundredth (0.77). The occupancy of La1A was then fixed to the remaining balance (0.23). Further disorder related to the conversion of **1** to **2** was modeled using the same ratio of occupancies. Least-squares analysis yielded wR_2 = 0.1095 and Goof = 1.070 for 870 variables refined against 14822 data (0.79 Å), R1 = 0.0439 for those 13185 data with I > 2.0σ(I).

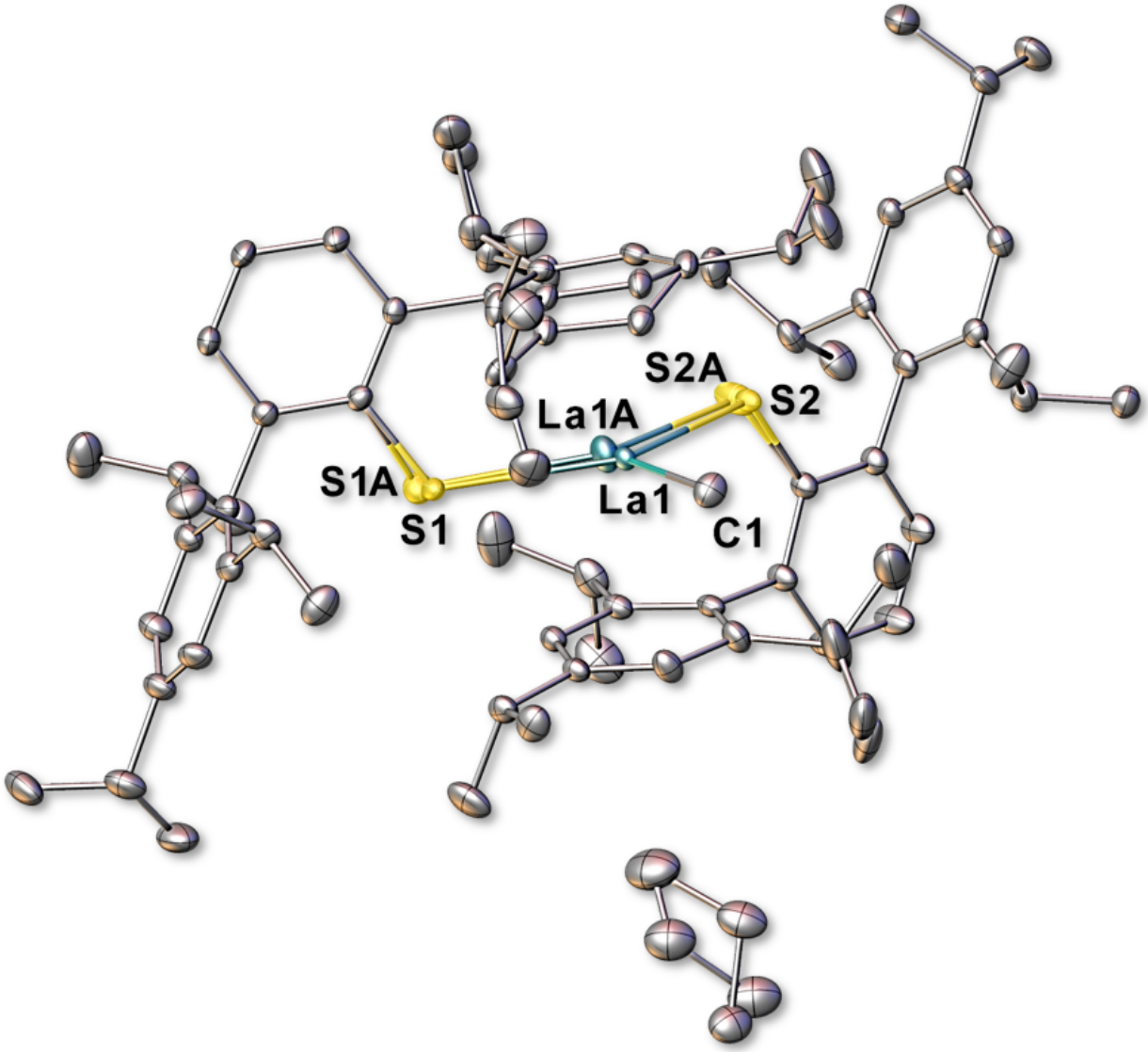

Figure S7. The molecular structure of a second crystal of La(SAr^{iPr6})$_2$CH$_3$, **1**, showing the conversion of **1** to **2** after 10 h and 24 min of data collection using Cu Kα X-rays. Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms are not shown. The occupancies of La1, C1, S1, and S2 are 77%, while the occupancies of La1A, S1A, and S2A are 23%. The occupancies of the affected carbons of the disordered flanking ring have been fixed to the same ratio in the model.

Table S8. X-ray data collection parameters and crystallographic details for a second crystal of La(SAr^{iPr6})$_2$CH$_3$·0.5(C_6H_{14}), **1 · 0.5(C_6H_{14})**. These data were collected using Cu Kα X-rays over a period of 5h and 12 min (total exposure to Cu Kα rays of 15h and 36 min).

Note: Fractional values for C and H are given in the following formula due to the partial occupancy of the methyl carbon bound to lanthanum that results from the formation of La(SAr^{iPr6})$_2$, **2**, under the conditions of the diffraction experiment.

Empirical formula	$LaS_2C_{75.65}H_{106.95}$
Formula weight	1219.39
Temperature/K	100.00
Crystal system	monoclinic
Space group	C2/c
a/Å	21.1319(5)
b/Å	18.3028(4)
c/Å	36.1912(10)
α/°	90
β/°	92.051(2)
γ/°	90
Volume/Å^3	13988.8(6)
Z	8
ρ_{calc}g/cm^3	1.158
μ/mm^{-1}	5.554
F(000)	5199.0
Crystal size/mm^3	0.116 × 0.09 × 0.087
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.886 to 158.43
Index ranges	-24 ≤ h ≤ 26, -23 ≤ k ≤ 21, -45 ≤ l ≤ 46
Reflections collected	114278
Independent reflections	14853 [R_{int} = 0.0734, R_{sigma} = 0.0391]
Data/restraints/parameters	14853/163/869
Goodness-of-fit on F^2	1.086
Final R indexes [I>=2σ (I)]	R_1 = 0.0567, wR_2 = 0.1356
Final R indexes [all data]	R_1 = 0.0688, wR_2 = 0.1428
Largest diff. peak/hole / e Å^{-3}	0.97/-0.62

X-ray Data Collection, Structure Solution and Refinement for a Second Crystal of La(SAr^{iPr6})$_2$CH$_3$·0.5(C_6H_{14}), 1 · 0.5(C_6H_{14}) (15 h and 36 min of X-ray Irradiation with Cu Kα X-rays).

Without disturbing the crystal from the prior experiment, data were collected again on this crystal using Cu Kα X-rays. As described above, the APEX5[5] program package was used to determine the unit-cell parameters and for data collection (4.5 sec/frame scan time). The raw frame data was processed using SAINT[6] and SADABS[7] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[8] program package. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space groups *Cc* and *C*2/*c*. It was later determined that space group C2/c was correct.

The structure was solved by direct methods and refined on F2 by full-matrix least-squares techniques. The analytical scattering factors[9] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The occupancies of the La, La1, and C1 atoms were first refined freely until a stable model was obtained and then the occupancies of the La1 and C1 atoms were fixed to the occupancy of the freely refined C1 atom and rounded to the nearest hundredth (0.65). The occupancy of La1A was then fixed to the remaining balance (0.35). Further disorder related to the conversion of **1** to **2** was modeled using the same ratio of occupancies. Least-squares analysis yielded wR_2 = 0.1428 and Goof = 1.086 for 869 variables refined against 14853 data (0.79 Å), R1 = 0.0567 for those 13185 data with I > 2.0σ(I).

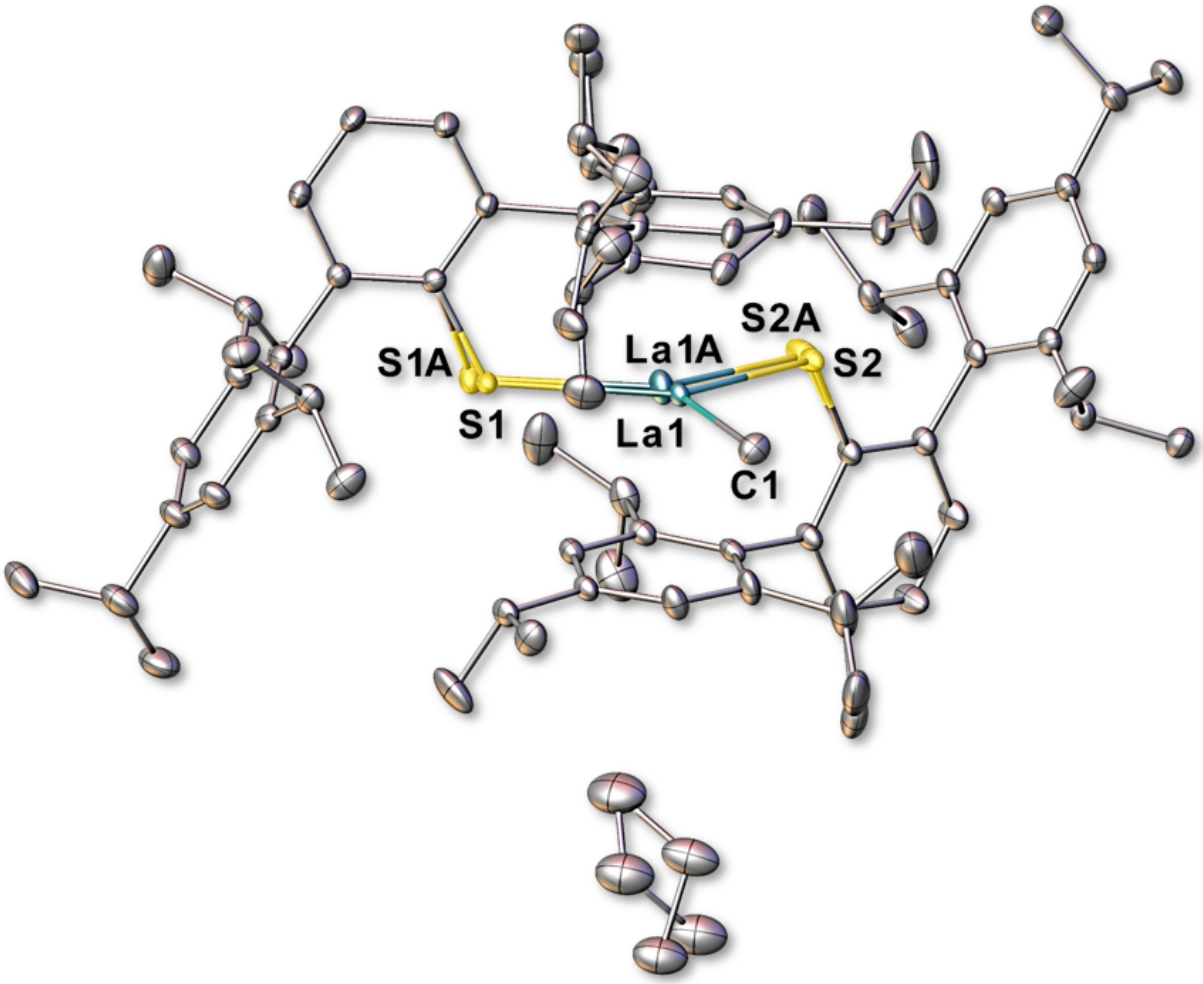

Figure S8. The molecular structure of a second crystal of La(SAr^{iPr6})$_2$CH$_3$, **1**, showing the conversion of **1** to **2** after 15 h and 36 min of data collection using Cu Kα X-rays. Thermal ellipsoids are drawn at 20% probability. Hydrogen atoms are not shown. The occupancies of La1, C1, S1, and S2 are 65%, while the occupancies of La1A, S1A, and S2A are 35%. The occupancies of the affected carbons of the disordered flanking ring have been fixed to the same ratio in the model.

Table S9. X-ray data collection parameters and crystallographic details for a second crystal of La(SAr^{iPr6})$_2$CH$_3$·0.5(C_6H_{14}), **1 · 0.5(C_6H_{14})**. These data were collected using Cu Kα X-rays over a period of 5h and 12 min (total exposure to Cu Kα rays of 20h and 48 min).

Note: Fractional values for C and H are given in the following formula due to the partial occupancy of the methyl carbon bound to lanthanum that results from the formation of La(SAr^{iPr6})$_2$, **2**, under the conditions of the diffraction experiment.

Empirical formula	$LaS_2C_{72.5}H_{99.5}$
Formula weight	1174.05
Temperature/K	100.00
Crystal system	monoclinic
Space group	C2/c
a/Å	21.0954(5)
b/Å	18.3275(4)
c/Å	36.2468(11)
α/°	90
β/°	92.474(2)
γ/°	90
Volume/Å^3	14000.9(6)
Z	8
ρ_{calc}g/cm^3	1.114
μ/mm^{-1}	5.532
F(000)	4988.0
Crystal size/mm^3	0.116 × 0.09 × 0.087
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.88 to 158.508
Index ranges	-23 ≤ h ≤ 26, -23 ≤ k ≤ 21, -45 ≤ l ≤ 46
Reflections collected	115171
Independent reflections	14947 [R_{int} = 0.0880, R_{sigma} = 0.0460]
Data/restraints/parameters	14947/179/855
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0624, wR_2 = 0.1388
Final R indexes [all data]	R_1 = 0.0826, wR_2 = 0.1491
Largest diff. peak/hole / e Å^{-3}	0.72/-0.49

X-ray Data Collection, Structure Solution and Refinement for a Second Crystal of La(SAr^{iPr6})$_2$CH$_3$·0.5(C$_6$H$_{14}$), 1 · 0.5(C$_6$H$_{14}$) (20 h and 48 min of X-ray Irradiation with Cu Kα X-rays).

Without disturbing the crystal from the prior experiment, data were collected again on this crystal using Cu Kα X-rays. As described above, the APEX5[5] program package was used to determine the unit-cell parameters and for data collection (4.5 sec/frame scan time). The raw frame data was processed using SAINT[6] and SADABS[7] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[8] program package. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space groups *Cc* and *C*2/*c*. It was later determined that space group C2/c was correct.

The structure was solved by direct methods and refined on F2 by full-matrix least-squares techniques. The analytical scattering factors[9] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The occupancies of the La, La1, and C1 atoms were first refined freely until a stable model was obtained and then the occupancies of the La1 and C1 atoms were fixed to the occupancy of the freely refined C1 atom and rounded to the nearest hundredth (0.50). The occupancy of La1A was then fixed to the remaining balance (0.50). Further disorder related to the conversion of **1** to **2** was modeled using the same ratio of occupancies. The disordered half molecule of hexane was excluded from refinement using SQUEEZE.[10] Least-squares analysis yielded wR_2 = 0.1491 and Goof = 1.060 for 855 variables refined against 14947 data (0.79 Å), R1 = 0.0624 for those 11267 data with I > 2.0σ(I).

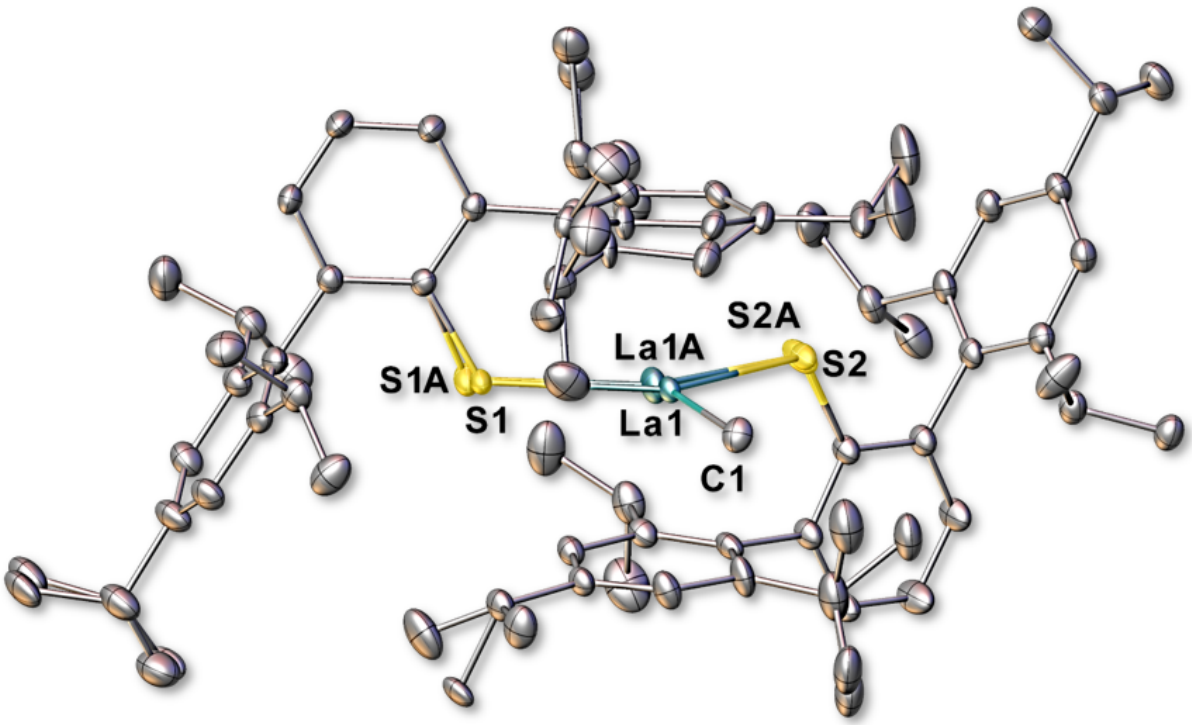

Figure S9. The molecular structure of a second crystal of La(SAr^{iPr6})$_2$CH$_3$, **1**, showing the conversion of **1** to **2** after 20 h and 48 min of data collection using Cu Kα X-rays. Thermal ellipsoids are drawn at 20% probability. Hydrogen atoms are not shown. The occupancies of La1, C1, S1, and S2 are 50%, while the occupancies of La1A, S1A, and S2A are 50%. The occupancies of the affected carbons of the disordered flanking ring have been fixed to the same ratio in the model.

Table S10. X-ray data collection parameters and crystallographic details for a second crystal of La(SAr^{iPr6})$_2$CH$_3$·0.5(C_6H_{14}), **1 · 0.5(C_6H_{14})**. These data were collected using Cu Kα X-rays over a period of 5h and 12 min (total exposure to Cu Kα rays of 26 h).

Note: Fractional values for C and H are given in the following formula due to the partial occupancy of the methyl carbon bound to lanthanum that results from the formation of La(SAr^{iPr6})$_2$, **2**, under the conditions of the diffraction experiment.

Empirical formula	$LaS_2C_{75.43}H_{106.29}$
Formula weight	1216.08
Temperature/K	100.00
Crystal system	monoclinic
Space group	C2/c
a/Å	21.0838(4)
b/Å	18.3446(3)
c/Å	36.2906(10)
α/°	90
β/°	92.716(2)
γ/°	90
Volume/Å^3	14020.5(5)
Z	8
ρ_{calc}g/cm^3	1.152
μ/mm^{-1}	5.540
F(000)	5183.0
Crystal size/mm^3	0.116 × 0.09 × 0.087
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.876 to 158.176
Index ranges	-23 ≤ h ≤ 26, -23 ≤ k ≤ 21, -45 ≤ l ≤ 46
Reflections collected	111561
Independent reflections	14981 [R_{int} = 0.0965, R_{sigma} = 0.0498]
Data/restraints/parameters	14981/331/920
Goodness-of-fit on F^2	1.085
Final R indexes [I>=2σ (I)]	R_1 = 0.0650, wR_2 = 0.1450
Final R indexes [all data]	R_1 = 0.0991, wR_2 = 0.1619
Largest diff. peak/hole / e Å^{-3}	0.56/-0.48

X-ray Data Collection, Structure Solution and Refinement for a Second Crystal of La(SAr^{iPr6})$_2$CH$_3$·0.5(C$_6$H$_{14}$), 1 · 0.5(C$_6$H$_{14}$) (26 h of X-ray Irradiation with Cu Kα X-rays).

Without disturbing the crystal from the prior experiment, data were collected again on this crystal using Cu Kα X-rays. As described above, the APEX5[5] program package was used to determine the unit-cell parameters and for data collection (4.5 sec/frame scan time). The raw frame data was processed using SAINT[6] and SADABS[7] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[8] program package. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space groups *Cc* and *C*2/*c*. It was later determined that space group C2/c was correct.

The structure was solved by direct methods and refined on F2 by full-matrix least-squares techniques. The analytical scattering factors[9] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The occupancies of the La, La1, and C1 atoms were first refined freely until a stable model was obtained and then the occupancies of the La1 and C1 atoms were fixed to the occupancy of the freely refined C1 atom and rounded to the nearest hundredth (0.43). The occupancy of La1A was then fixed to the remaining balance (0.57). Further disorder related to the conversion of **1** to **2** was modeled using the same ratio of occupancies. Least-squares analysis yielded wR_2 = 0.1619 and Goof = 1.085 for 920 variables refined against 14981 data (0.79 Å), R1 = 0.0650 for those 10019 data with I > 2.0σ(I).

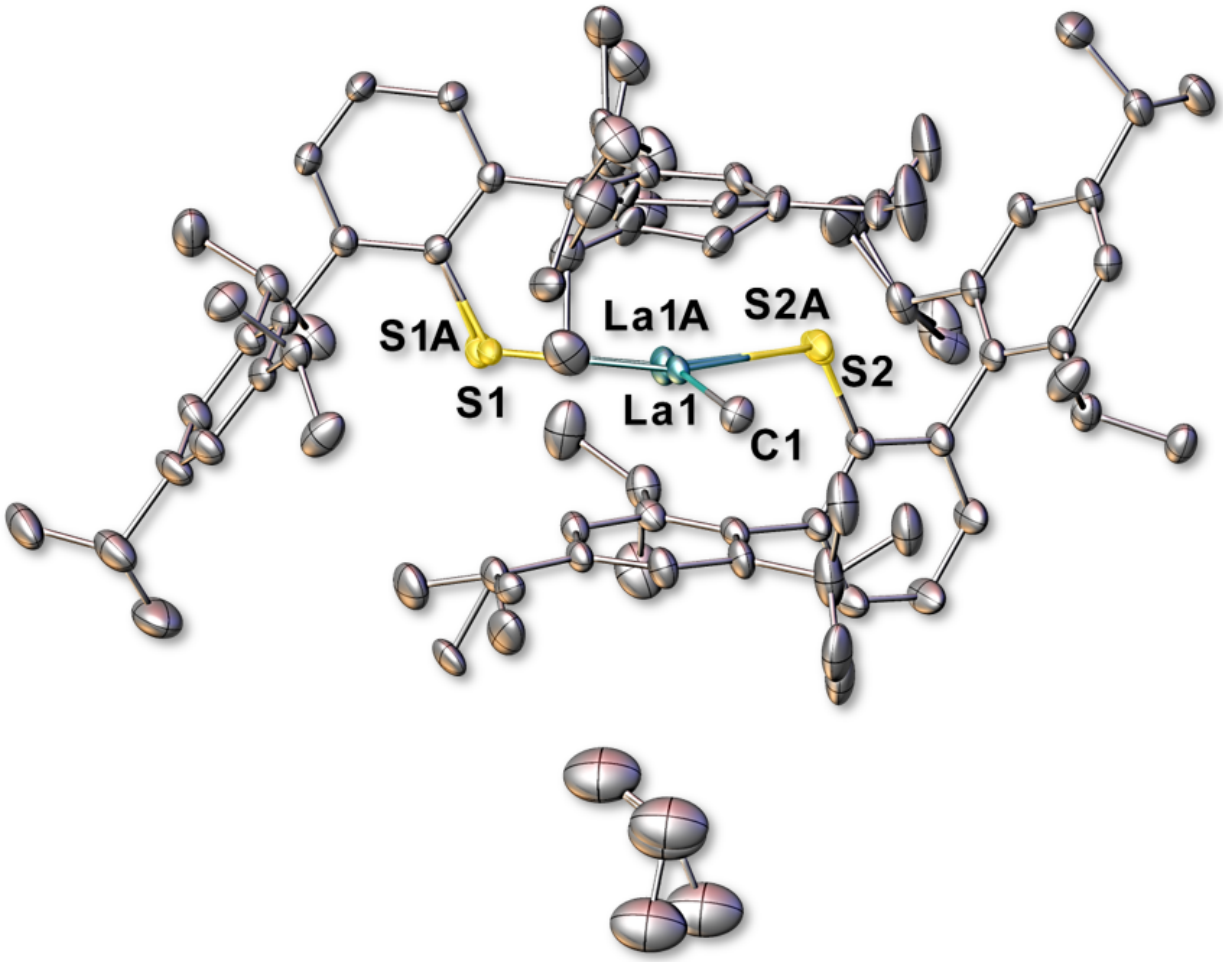

Figure S10. The molecular structure of a second crystal of La(SAr^{iPr6})$_2$CH$_3$, **1**, showing the conversion of **1** to **2** after 26 h of data collection using Cu Kα X-rays. Thermal ellipsoids are drawn at 20% probability. Hydrogen atoms are not shown. The occupancies of La1, C1, S1, and S2 are 43%, while the occupancies of La1A, S1A, and S2A are 57%. The occupancies of the affected carbons of the disordered flanking ring have been fixed to the same ratio in the model.

Table S11. X-ray data collection parameters and crystallographic details for a second crystal of La(SAr^{iPr6})$_2$CH$_3$·0.5(C_6H_{14}), **1 · 0.5(C_6H_{14})**. These data were collected using Cu Kα X-rays over a period of 5h and 12 min (total exposure to Cu Kα rays of 31 h and 12 min).

Note: Fractional values for C and H are given in the following formula due to the partial occupancy of the methyl carbon bound to lanthanum that results from the formation of La(SAr^{iPr6})$_2$, **2**, under the conditions of the diffraction experiment.

Empirical formula	$LaS_2C_{72.36}H_{99.08}$
Formula weight	1171.94
Temperature/K	100.00
Crystal system	monoclinic
Space group	C2/c
a/Å	21.0557(7)
b/Å	18.3608(6)
c/Å	36.3221(14)
α/°	90
β/°	92.851(3)
γ/°	90
Volume/Å^3	14024.7(8)
Z	8
ρ_{calc}g/cm^3	1.110
μ/mm^{-1}	5.522
F(000)	4978.0
Crystal size/mm^3	0.116 × 0.09 × 0.087
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.872 to 159.978
Index ranges	-23 ≤ h ≤ 26, -23 ≤ k ≤ 21, -45 ≤ l ≤ 46
Reflections collected	112266
Independent reflections	14957 [R_{int} = 0.1201, R_{sigma} = 0.0592]
Data/restraints/parameters	14957/386/895
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0743, wR_2 = 0.1680
Final R indexes [all data]	R_1 = 0.1194, wR_2 = 0.1915
Largest diff. peak/hole / e Å^{-3}	0.45/-0.51

X-ray Data Collection, Structure Solution and Refinement for a Second Crystal of La(SAr^{iPr6})$_2$CH$_3$·0.5(C_6H_{14}), 1 · 0.5(C_6H_{14}) (31 h and 12 min of X-ray Irradiation with Cu Kα X-rays).

Without disturbing the crystal from the prior experiment, data were collected again on this crystal using Cu Kα X-rays. As described above, the APEX5[5] program package was used to determine the unit-cell parameters and for data collection (4.5 sec/frame scan time). The raw frame data was processed using SAINT[6] and SADABS[7] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[8] program package. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space groups *Cc* and *C*2/*c*. It was later determined that space group C2/c was correct.

The structure was solved by direct methods and refined on F2 by full-matrix least-squares techniques. The analytical scattering factors[9] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The occupancies of the La, La1, and C1 atoms were first refined freely until a stable model was obtained and then the occupancies of the La1 and C1 atoms were fixed to the occupancy of the freely refined C1 atom and rounded to the nearest hundredth (0.36). The occupancy of La1A was then fixed to the remaining balance (0.64). Further disorder related to the conversion of **1** to **2** was modeled using the same ratio of occupancies. The disordered half molecule of hexane was excluded from refinement using SQUEEZE.[10] Least-squares analysis yielded wR_2 = 0.1915 and Goof = 1.038 for 895 variables refined against 14957 data (0.79 Å), R1 = 0.0743 for those 8772 data with I > 2.0σ(I).

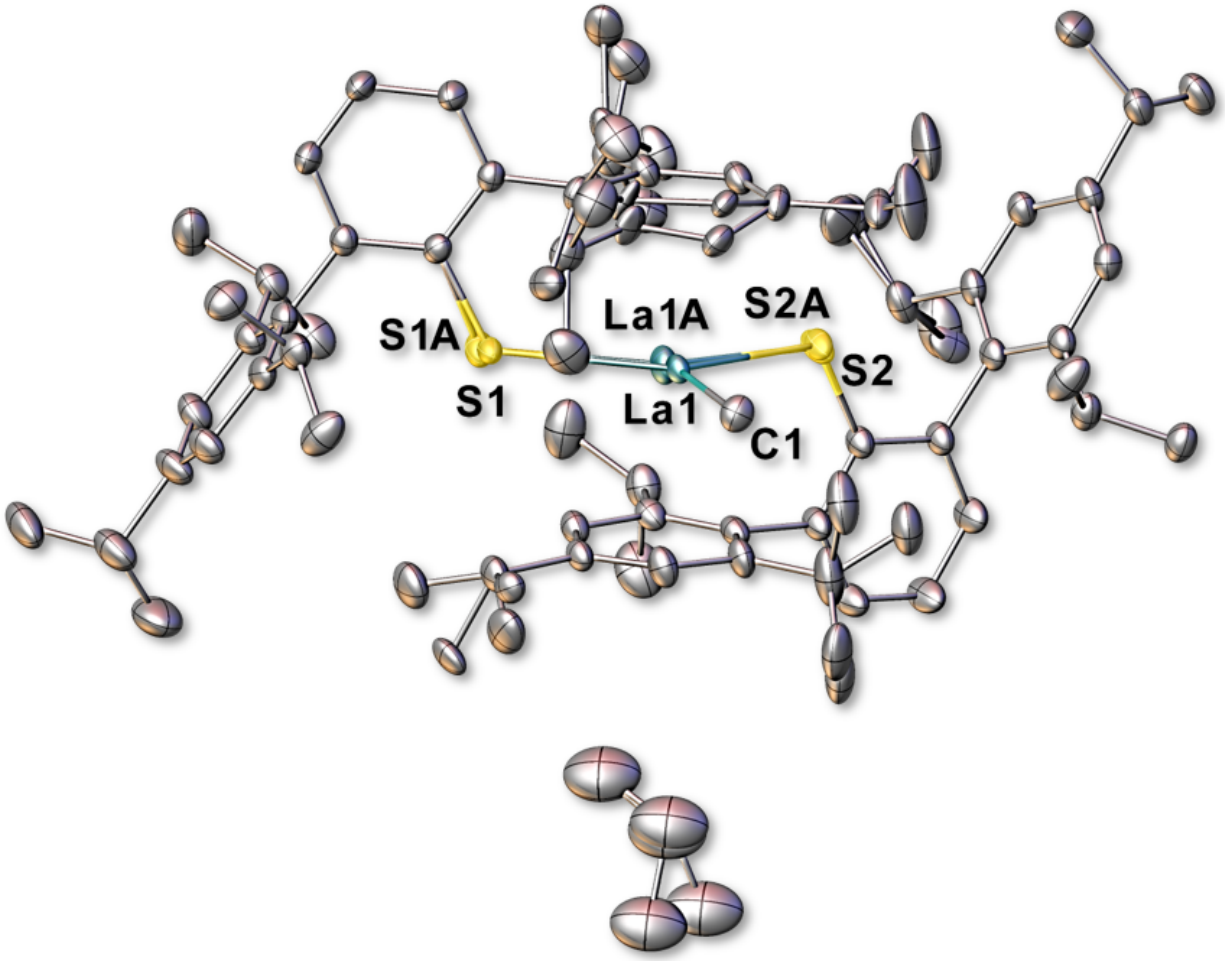

Figure S11. The molecular structure of a second crystal of La(SAr^{iPr6})$_2$CH$_3$, **1**, showing the conversion of **1** to **2** after 31 h and 12 min of data collection using Cu Kα X-rays. Thermal ellipsoids are drawn at 20% probability. Hydrogen atoms are not shown. The occupancies of La1, C1, S1, and S2 are 36%, while the occupancies of La1A, S1A, and S2A are 64%. The occupancies of the affected carbons of the disordered flanking ring have been fixed to the same ratio in the model.

Table S12. X-ray data collection parameters and crystallographic details for a second crystal of La(SAr^{iPr6})$_2$CH$_3$·0.5(C_6H_{14}), **1 · 0.5(C_6H_{14})**. These data were collected using Cu Kα X-rays over a period of 5h and 12 min (total exposure to Cu Kα rays of 36 h and 24 min).

Note: Fractional values for C and H are given in the following formula due to the partial occupancy of the methyl carbon bound to lanthanum that results from the formation of La(SAr^{iPr6})$_2$, **2**, under the conditions of the diffraction experiment.

Empirical formula	$LaS_2C_{72.31}H_{98.93}$
Formula weight	1171.19
Temperature/K	100.00
Crystal system	monoclinic
Space group	C2/c
a/Å	20.9956(13)
b/Å	18.3324(12)
c/Å	36.449(3)
α/°	90
β/°	93.160(5)
γ/°	90
Volume/Å^3	14007.9(16)
Z	8
ρ_{calc}g/cm^3	1.111
μ/mm^{-1}	5.529
F(000)	4974.0
Crystal size/mm^3	0.116 × 0.09 × 0.087
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.856 to 159.15
Index ranges	-23 ≤ h ≤ 26, -23 ≤ k ≤ 21, -45 ≤ l ≤ 45
Reflections collected	101159
Independent reflections	14773 [R_{int} = 0.1523, R_{sigma} = 0.0774]
Data/restraints/parameters	14773/502/910
Goodness-of-fit on F^2	1.015
Final R indexes [I>=2σ (I)]	R_1 = 0.0746, wR_2 = 0.1686
Final R indexes [all data]	R_1 = 0.1461, wR_2 = 0.2039
Largest diff. peak/hole / e Å^{-3}	0.39/-0.45

X-ray Data Collection, Structure Solution and Refinement for a Second Crystal of La(SAr^{iPr6})$_2$CH$_3$·0.5(C_6H_{14}), 1 · 0.5(C_6H_{14}) (36 h and 24 min of X-ray Irradiation with Cu Kα X-rays).

Without disturbing the crystal from the prior experiment, data were collected again on this crystal using Cu Kα X-rays. As described above, the APEX5[5] program package was used to determine the unit-cell parameters and for data collection (4.5 sec/frame scan time). The raw frame data was processed using SAINT[6] and SADABS[7] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[8] program package. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space groups *Cc* and *C*2/*c*. It was later determined that space group C2/c was correct.

The structure was solved by direct methods and refined on F2 by full-matrix least-squares techniques. The analytical scattering factors[9] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The occupancies of the La, La1, and C1 atoms were first refined freely until a stable model was obtained and then the occupancies of the La1 and C1 atoms were fixed to the occupancy of the freely refined C1 atom and rounded to the nearest hundredth (0.31). The occupancy of La1A was then fixed to the remaining balance (0.69). Further disorder related to the conversion of **1** to **2** was modeled using the same ratio of occupancies. The disordered half molecule of hexane was excluded from refinement using SQUEEZE.[10] Least-squares analysis yielded wR_2 = 0.1915 and Goof = 1.038 for 895 variables refined against 14957 data (0.79 Å), R1 = 0.0743 for those 8772 data with I > 2.0σ(I).

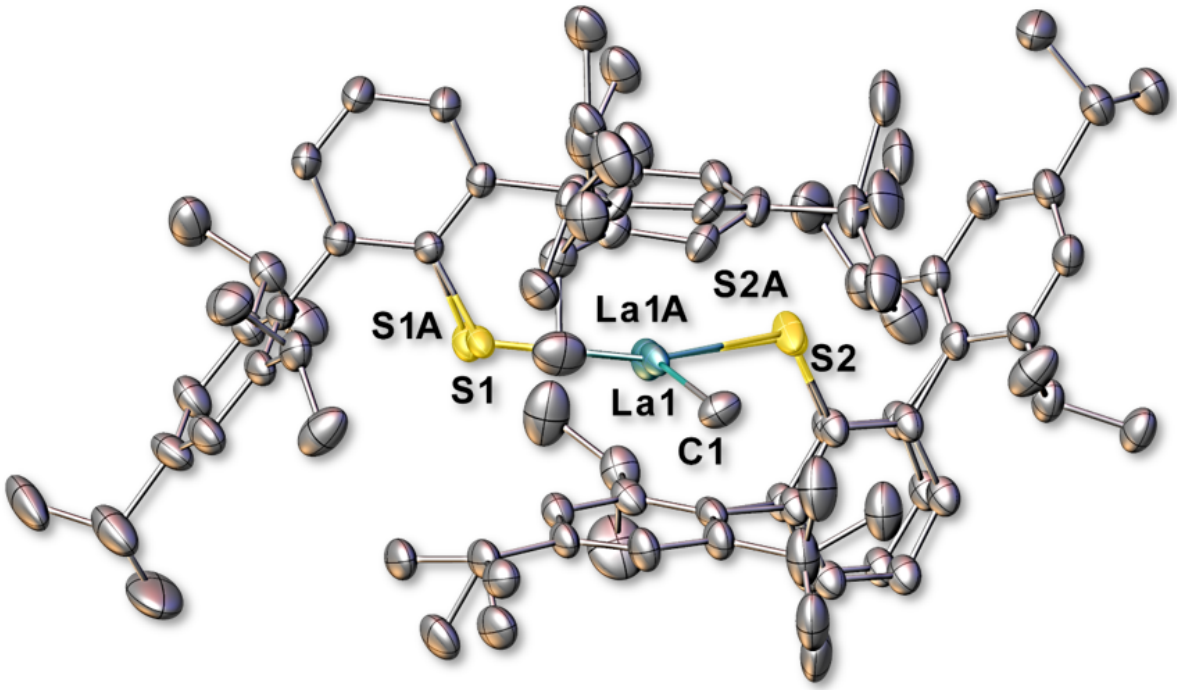

Figure S12. The molecular structure of a second crystal of La(SAr^{iPr6})$_2$CH$_3$, **1**, showing the conversion of **1** to **2** after 36 h and 24 min of data collection using Cu Kα X-rays. Thermal ellipsoids are drawn at 20% probability. Hydrogen atoms are not shown. The occupancies of La1, C1, S1, and S2 are 31%, while the occupancies of La1A, S1A, and S2A are 69%. The occupancies of the affected carbons of the disordered flanking ring have been fixed to the same ratio in the model.

Table S13. X-ray data collection parameters and crystallographic details for a second crystal of La(SAr^{iPr6})$_2$CH$_3$·0.5(C_6H_{14}), **1 · 0.5(C_6H_{14})**. These data were collected using Cu Kα X-rays over a period of 5h and 12 min (total exposure to Cu Kα rays of 41 h and 36 min).

Note: Fractional values for C and H are given in the following formula due to the partial occupancy of the methyl carbon bound to lanthanum that results from the formation of La(SAr^{iPr6})$_2$, **2**, under the conditions of the diffraction experiment.

Empirical formula	$LaS_2C_{72.25}H_{98.75}$
Formula weight	1170.29
Temperature/K	100.00
Crystal system	monoclinic
Space group	C2/c
a/Å	21.0489(8)
b/Å	18.3665(6)
c/Å	36.3898(17)
α/°	90
β/°	93.102(3)
γ/°	90
Volume/Å^3	14047.5(10)
Z	8
ρ_{calc}g/cm^3	1.107
μ/mm^{-1}	5.513
F(000)	4970.0
Crystal size/mm^3	0.116 × 0.09 × 0.087
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.864 to 136.486
Index ranges	-23 ≤ h ≤ 24, -20 ≤ k ≤ 20, -40 ≤ l ≤ 36
Reflections collected	56233
Independent reflections	11752 [R_{int} = 0.1118, R_{sigma} = 0.0898]
Data/restraints/parameters	11752/481/890
Goodness-of-fit on F^2	1.002
Final R indexes [I>=2σ (I)]	R_1 = 0.0730, wR_2 = 0.1713
Final R indexes [all data]	R_1 = 0.1548, wR_2 = 0.2095
Largest diff. peak/hole / e Å^{-3}	0.49/-0.42

X-ray Data Collection, Structure Solution and Refinement for a Second Crystal of La(SAr^{iPr6})$_2$CH$_3$·0.5(C_6H_{14}), 1 · 0.5(C_6H_{14}) (41 h and 36 min of X-ray Irradiation with Cu Kα X-rays).

Without disturbing the crystal from the prior experiment, data were collected again on this crystal using Cu Kα X-rays. As described above, the APEX5[5] program package was used to determine the unit-cell parameters and for data collection (4.5 sec/frame scan time). The raw frame data was processed using SAINT[6] and SADABS[7] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[8] program package. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space groups *Cc* and *C*2/*c*. It was later determined that space group C2/c was correct.

The structure was solved by direct methods and refined on F2 by full-matrix least-squares techniques. The analytical scattering factors[9] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The occupancies of the La, La1, and C1 atoms were first refined freely until a stable model was obtained and then the occupancies of the La1 and C1 atoms were fixed to the occupancy of the freely refined C1 atom and rounded to the nearest hundredth (0.25). The occupancy of La1A was then fixed to the remaining balance (0.75). Further disorder related to the conversion of **1** to **2** was modeled using the same ratio of occupancies. The disordered half molecule of hexane was excluded from refinement using SQUEEZE.[10] Least-squares analysis yielded wR_2 = 0.2095 and Goof = 1.002 for 890 variables refined against 11752 data (0.79 Å), R1 = 0.0730 for those 5605 data with I > 2.0σ(I).

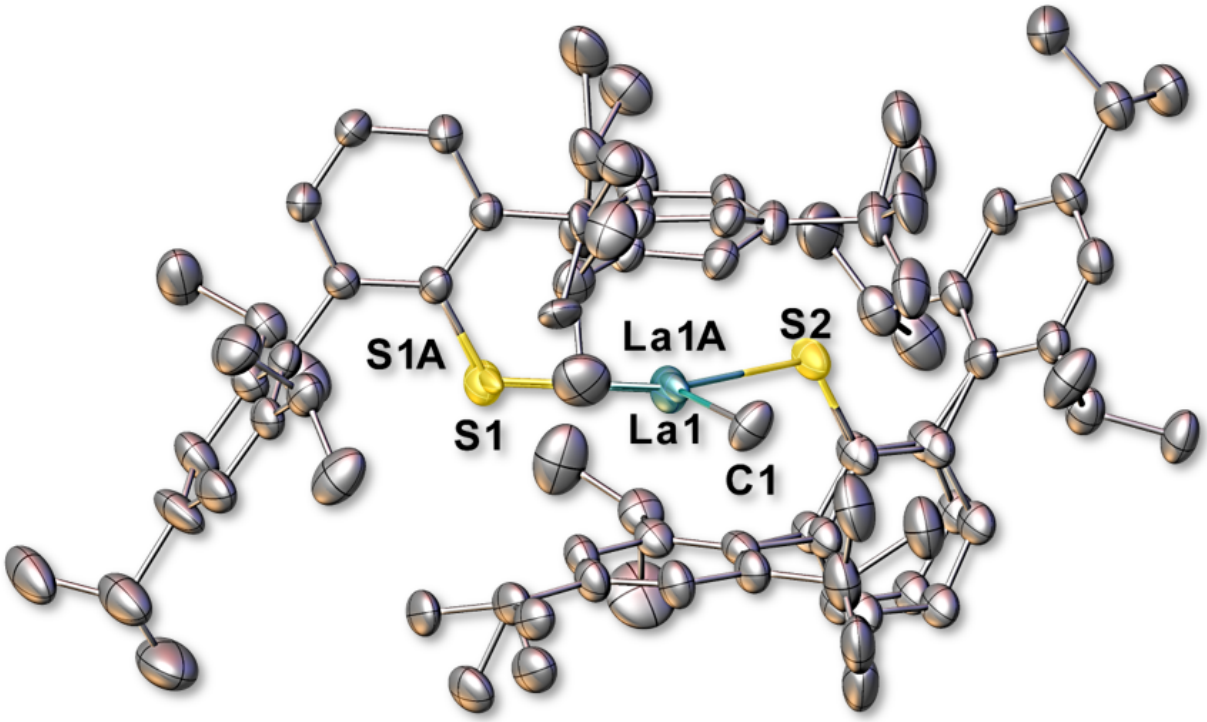

Figure S13. The molecular structure of a second crystal of La(SAr^{iPr6})$_2$CH$_3$, **1**, showing the conversion of **1** to **2** after 41 h and 36 min of data collection using Cu Kα X-rays. Thermal ellipsoids are drawn at 20% probability. Hydrogen atoms are not shown. The occupancies of La1, C1, S1, and S2 are 25%, while the occupancies of La1A, S1A, and S2A are 75%. The occupancies of the affected carbons of the disordered flanking ring have been fixed to the same ratio in the model.

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