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Sigma Bond Metathesis with Pentamethylcyclopentadienyl Ligands in Sterically Crowded $(C_5Me_5)_3M$ Complexes

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X-ray Data Collection, Structure Solution and Refinement for $[(C_5Me_5)_2La(SePh)]_2$, **1b**.

A colorless crystal of approximate dimensions 0.22 x 0.24 x 0.26 mm was mounted on a glass fiber and transferred to a Bruker SMART1K diffractometer. The SMART[1] program package was used to determine the unit-cell parameters and for data collection (25 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[2] and SADABS[3] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4] program. The diffraction symmetry was *mmm* and the systematic absences were consistent with the orthorhombic space groups *Pnn*2 *and Pnnm*. It was later determined that the noncentrosymmetric space group *Pnn*2 was correct.

The structure was solved using the coordinates of the cerium sulfur analogue and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[5] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecule is located on a two-fold rotation axis.

At convergence, wR2 = 0.0460 and Goof = 1.057 for 265 variables refined against 6015 data (0.75Å), R1 = 0.0187 for those 5560 data with $I > 2.0\sigma(I)$. The structure was refined as a twin with the Flack[6] parameter/BASF = 0.232(9).

[1] SMART Software Users Guide, Version 5.1, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 1999.
[2] SAINT Version 6.36a, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 1999.
[3] Sheldrick, G. M. SADABS, Version 2008/1, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 2008.
[4] Sheldrick, G. M. SHELXTL Version 6.12, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 2001.
[5] International Tables for X-Ray Crystallography 1992, Vol. C., Dordrecht: Kluwer Academic Publishers.
[6] H. D. Flack, *Acta. Cryst.*, 1983, **A39**, 876.

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Table 1. Crystal data and structure refinement for **1b**.

Identification code	tjm4 (**1b**)	
Empirical formula	$C_{52}H_{70}La_2Se_2$	
Formula weight	1130.82	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	*Pnn*2	
Unit cell dimensions	a = 10.3729(10) Å	α= 90°.
	b = 12.0187(12) Å	β= 90°.
	c = 19.4835(19) Å	γ = 90°.
Volume	2429.0(4) $Å^3$	
Z	2	
Density (calculated)	1.546 Mg/m^3	
Absorption coefficient	3.266 mm^{-1}	
F(000)	1128	
Crystal color	colorless	
Crystal size	0.26 x 0.24 x 0.22 mm^3	
Theta range for data collection	1.99 to 28.30°	
Index ranges	$-13 \le h \le 13$, $-15 \le k \le 16$, $-25 \le l \le 25$	
Reflections collected	25662	
Independent reflections	6015 [R(int) = 0.0258]	
Completeness to theta = 28.30°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5336 and 0.4839	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6015 / 1 / 265	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I) = 5560 data]	R1 = 0.0187, wR2 = 0.0445	
R indices (all data, 0.75Å)	R1 = 0.0221, wR2 = 0.0460	
Absolute structure parameter	0.232(9)	
Largest diff. peak and hole	0.487 and -0.599 $e.Å^{-3}$	

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,z

X-ray Data Collection, Structure Solution and Refinement for $[(C_5Me_5)_2La(SePh)(NCCMe_3)]_2$, **2b**.

A colorless crystal of approximate dimensions 0.09 x 0.19 x 0.34 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2[7] program package was used to determine the unit-cell parameters and for data collection (25 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[8] and SADABS[9] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4] program. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[5] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecules were dimers and were located about inversion centers. There were 3.5 molecules of benzene solvent present per dimeric formula-unit. At convergence, wR2 = 0.0583 and Goof = 1.023 for 828 variables refined against 17502 data (0.74Å), R1 = 0.0237 for those 15175 data with $I > 2.0\sigma(I)$.

[7] APEX2 Version 2.2-0 Bruker AXS, Inc.; Madison, WI 2007.
[8] SAINT Version 7.46a, Bruker AXS, Inc.; Madison, WI 2007
[9] Sheldrick, G. M. SADABS, Version 2007/4, Bruker AXS, Inc.; Madison, WI 2007

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Table 2. Crystal data and structure refinement for **2b**.

Identification code	tjm30 (**2b**)	
Empirical formula	$C_{62}H_{88}La_2N_2Se_2 \bullet 3.5(C_6H_6)$	
Formula weight	1570.46	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 14.9927(9) Å	α= 88.5675(7)°.
	b = 15.3140(9) Å	β= 88.8528(7)°.
	c = 16.9117(10) Å	γ = 79.9654(7)°.
Volume	3821.8(4) $Å^3$	
Z	2	
Density (calculated)	1.365 Mg/m^3	
Absorption coefficient	2.098 mm^{-1}	
F(000)	1606	
Crystal color	colorless	
Crystal size	0.34 x 0.19 x 0.09 mm^3	
Theta range for data collection	1.75 to 28.50°	
Index ranges	$-20 \le h \le 19$, $-20 \le k \le 20$, $-22 \le l \le 22$	
Reflections collected	44479	
Independent reflections	17502 [R(int) = 0.0210]	
Completeness to theta = 28.50°	90.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8337 and 0.5357	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	17502 / 0 / 828	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I) = 15175 data]	R1 = 0.0237, wR2 = 0.0558	
R indices (all data)	R1 = 0.0305, wR2 = 0.0583	
Largest diff. peak and hole	0.853 and -0.464 $e.Å^{-3}$	

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+1 #2 -x+2,-y+1,-z #3 -x+1,-y+1,-z+1

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X-ray Data Collection, Structure Solution and Refinement for $[(C_5Me_5)_2Ce(SPh)]_2$, **3**, Figure S1.

A purple crystal of approximate dimensions 0.19 x 0.21 x 0.32 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2[10] program package was used to determine the unit-cell parameters and for data collection (20 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[11] and SADABS[3] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4] program. The diffraction symmetry was *mmm* and the systematic absences were consistent with the orthorhombic space groups *Pnn*2 *and Pnnm*. It was later determined that the noncentrosymmetric space group *Pnn*2 was correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[5] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecule was located on a two-fold rotation axis.

At convergence, wR2 = 0.0584 and Goof = 1.046 for 264 variables refined against 5782 data (0.75Å), R1 = 0.0207 for those 5498 data with $I > 2.0\sigma(I)$. The absolute structure was assigned by refinement of the Flack parameter.[6]

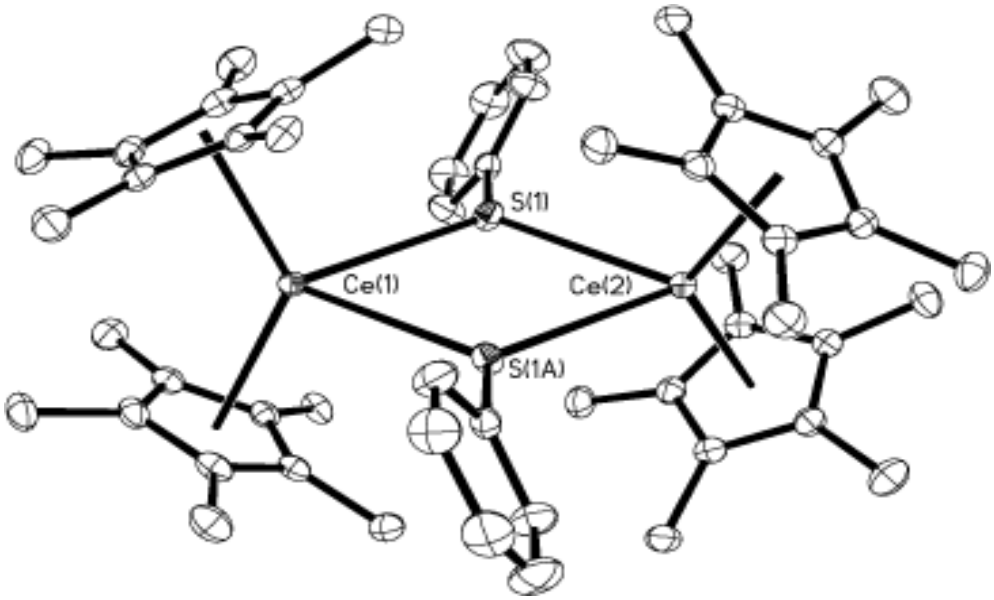

Figure S1. Thermal ellipsoid plot of $[(C_5Me_5)_2Ce(SPh)]_2$, **3**, drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

[10] APEX2 Version 2008.3-0, Bruker AXS, Inc.; Madison, WI 200/8.
[11] SAINT Version 7.53a, Bruker AXS, Inc.; Madison, WI 2007.

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

Identification code	tjm29 (**3**)	
Empirical formula	$C_{52}\ H_{70}\ Ce_2\ S_2$	
Formula weight	1039.44	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	*Pnn*2	
Unit cell dimensions	a = 10.3287(7) Å	α= 90°.
	b = 11.7979(8) Å	β= 90°.
	c = 19.4736(13) Å	γ = 90°.
Volume	2373.0(3) $Å^3$	
Z	2	
Density (calculated)	1.455 Mg/m^3	
Absorption coefficient	2.015 mm^{-1}	
F(000)	1060	
Crystal color	purple	
Crystal size	0.32 x 0.21 x 0.19 mm^3	
Theta range for data collection	2.02 to 28.28°	
Index ranges	$-13 \le h \le 13$, $-15 \le k \le 15$, $-25 \le l \le 25$	
Reflections collected	26891	
Independent reflections	5782 [R(int) = 0.0247]	
Completeness to theta = 28.28°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7008 and 0.5649	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5782 / 1 / 264	
Goodness-of-fit on F^2	1.046	
Final R indices [I>2sigma(I) = 5498 data]	R1 = 0.0207, wR2 = 0.0571	
R indices (all data, 0.75Å)	R1 = 0.0218, wR2 = 0.0584	
Absolute structure parameter	0.001(14)	
Largest diff. peak and hole	1.152 and -0.276 $e.Å^{-3}$	

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,z

X-ray Data Collection, Structure Solution and Refinement for $[(C_5Me_5)_2Pr(SPh)]_2$, **5**, Figure S2.

A yellow crystal of approximate dimensions 0.13 x 0.15 x 0.18 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2[7] program package was used to determine the unit-cell parameters and for data collection (10 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[8] and SADABS[3] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[12] program. The diffraction symmetry was *mmm* and the systematic absences were consistent with the orthorhombic space groups *Pnn*2 *and Pnnm*. It was later determined that the noncentrosymmetric space group *Pnn*2 was correct.

The structure was solved using the coordinates of the analogous cerium complex and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[5] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecule was located on a two-fold rotation axis.

At convergence, wR2 = 0.0930 and Goof = 1.028 for 264 variables refined against 5403 data (0.77Å), R1 = 0.0334 for those 4399 data with $I > 2.0\sigma(I)$. The absolute structure was assigned by refinement of the Flack parameter.[6]

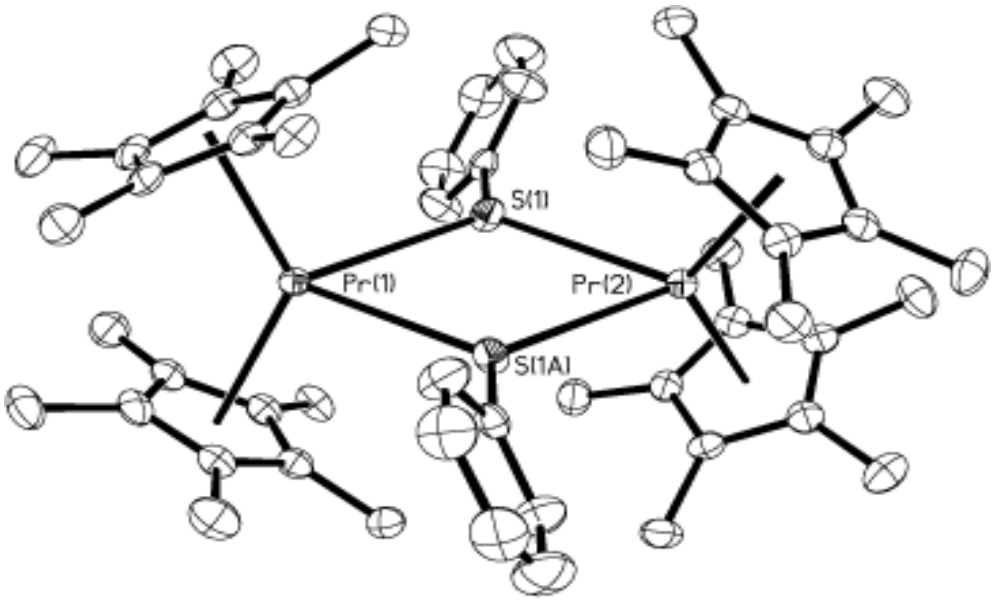

Figure S2. Thermal ellipsoid plot of $[(C_5Me_5)_2Pr(SPh)]_2$, **5**, drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

[12] Sheldrick, G. M. SHELXTL, Version 2008/3, Bruker AXS, Inc.; Madison, WI 2008.

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Table 4. Crystal data and structure refinement for $[(C_5Me_5)_2Pr(SPh)]_2$, **5**.

Identification code	tjm35 (**5**)	
Empirical formula	$C_{52}\ H_{70}\ Pr_2\ S_2$	
Formula weight	1041.02	
Temperature	148(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	*Pnn*2	
Unit cell dimensions	a = 10.3504(6) Å	α= 90°.
	b = 11.7647(7) Å	β= 90°.
	c = 19.4542(12) Å	γ = 90°.
Volume	2368.9(2) $Å^3$	
Z	2	
Density (calculated)	1.459 Mg/m^3	
Absorption coefficient	2.153 mm^{-1}	
F(000)	1064	
Crystal color	yellow	
Crystal size	0.18 x 0.15 x 0.13 mm^3	
Theta range for data collection	2.02 to 27.48°	
Index ranges	$-13 \le h \le 13$, $-15 \le k \le 15$, $-25 \le l \le 25$	
Reflections collected	25686	
Independent reflections	5403 [R(int) = 0.0477]	
Completeness to theta = 27.48°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7671 and 0.6979	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5403 / 1 / 264	
Goodness-of-fit on F^2	1.028	
Final R indices [I>2sigma(I) = 4399 data]	R1 = 0.0334, wR2 = 0.0859	
R indices (all data, 0.77Å)	R1 = 0.0434, wR2 = 0.0930	
Absolute structure parameter	-0.01(3)	
Largest diff. peak and hole	2.663 and -0.492 $e.Å^{-3}$	

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,z