Supporting Information

[Ru$_6$(μ_6-Sb)(CO)$_{18}$]$^{3-}$: Deeply Reduced Metal Carbonyl Cluster

Embedded with Naked μ_6-Sb

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Contents

1. Material characterizations

All manipulations and reactions were performed in nitrogen atmosphere by using standard Schlenk and glove box techniques. Solvents were purified, dried, distilled, and stored in the glove box prior to use. Electrospray mass spectra were recorded from DMF solutions of **1** with nitrogen as sheath gas flow on a Finnigan LCQ-Ion Trap Mass Spectrometer (LCQ DECAX-30000 LCQ Deca XP) in negative-ion mode (spray voltage 4.5kV, capillary temperature 275 ℃ capillary voltage 15V). The sample was made inside a glovebox under an inert atmosphere and rapidly transferred to the spectrometer in an air-tight syringe by direct infusion with a Harvard syringe pump at 15 mL/min. The intensity data were collected on a Saturn724 (2 × 2 bin mode) diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å) at room temperature. The structure was solved by direct methods and

refined by full-matrix least-squares on F^2 with the SHELXTL-97 program package.

2. Crystallographic data

Table S1. X-ray crystallographic data for **1**.

Compound	1
Empirical formula	$C_{86}H_{121}K_3 N_6O_{36}Ru_6Sb$
Formula weight	2660.36
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$Pna2_1$
Unit cell dimensions	a = 19.7255(5) Å b = 25.5075(6) Å c = 21.1380(7) Å
Volume	10635.5(5) Å3
Z	4
Density (calculated)	1.661 Mg/m3
Absorption coefficient	1.277 mm-1
F(000)	5356
θ range	2.19 to 27.48
Index ranges	-25≤ h ≤25 -33≤ k ≤33 -27≤ l ≤27
Independent reflection	24236 [R(int) = 0.0398]
Reflections (> 2σ(I))	23602
Completeness	99.7 %
Flack	0.00(12)
Goodness-of-fit on F^2	1.07
R_1/wR$_2$ indices [I>2σ(I)]	0.0478/0.1054

R$_1$/wR$_2$ indices (all data)	0.0493/0.1064

$R_1=\sum||Fo|-|Fc||/\sum|Fo|$; $wR_2=\{\sum[w(Fo^2-Fc^2)^2]/\sum[w(Fo^2)^2]\}1/2$

Table S2. Selected bond lengths (Å) and angles (°) of **1**.

Sb-Ru(6)	2.5547(6)
Sb-Ru(1)	2.5621(6)
Sb-Ru(5)	2.6952(5)
Sb-Ru(2)	2.6960(6)
Sb-Ru(3)	2.8463(6)
Sb-Ru(4)	2.9040(6)
Ru(1)-C(6)	1.870(8)
Ru(1)-C(1)	1.901(8)
Ru(1)-C(7)	1.907(7)
Ru(1)-Ru(3)	2.9428(7)
Ru(1)-Ru(2)	2.9525(7)
Ru(3)-C(3)	1.874(8)
Ru(3)-C(14)	1.888(6)
Ru(3)-C(2)	1.926(7)
Ru(3)-C(11)	2.219(7)
Ru(3)-Ru(2)	2.8928(7)
Ru(3)-Ru(5)	3.1611(6)
Ru(2)-C(9)	1.846(7)
Ru(2)-C(18)	1.855(7)
Ru(2)-C(11)	1.970(7)
Ru(2)-Ru(5)	3.0957(7)
Ru(2)-Ru(4)	3.1451(7)
Ru(6)-C(4)	1.890(6)
Ru(6)-C(12)	1.893(7)
Ru(6)-C(15)	1.912(6)
Ru(6)-Ru(4)	2.9092(7)
Ru(6)-Ru(5)	2.9837(6)
Ru(5)-C(17)	1.850(7)
Ru(5)-C(16)	1.856(6)
Ru(5)-C(13)	1.974(6)
Ru(5)-Ru(4)	2.9004(6)
Ru(4)-C(8)	1.881(7)
Ru(4)-C(10)	1.882(7)
Ru(4)-C(5)	1.932(6)
Ru(4)-C(13)	2.207(5)
Ru(6)-Sb-Ru(1)	161.82(2)
Ru(6)-Sb-Ru(5)	69.209(17)
Ru(1)-Sb-Ru(5)	128.76(2)
Ru(6)-Sb-Ru(2)	127.41(2)
Ru(1)-Sb-Ru(2)	68.268(18)

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Ru(5)-Sb-Ru(2)	70.090(16)
Ru(6)-Sb-Ru(3)	127.31(2)
Ru(1)-Sb-Ru(3)	65.684(17)
Ru(5)-Sb-Ru(3)	69.497(15)
Ru(2)-Sb-Ru(3)	62.856(17)
Ru(6)-Sb-Ru(4)	64.033(17)
Ru(1)-Sb-Ru(4)	123.72(2)
Ru(5)-Sb-Ru(4)	62.265(15)
Ru(2)-Sb-Ru(4)	68.220(16)
Ru(3)-Sb-Ru(4)	119.771(17)
Sb-Ru(1)-Ru(3)	61.813(16)
Sb-Ru(1)-Ru(2)	58.018(15)
Ru(3)-Ru(1)-Ru(2)	58.771(16)
Sb-Ru(3)-Ru(2)	56.030(15)
Sb-Ru(3)-Ru(1)	52.503(15)
Ru(2)-Ru(3)-Ru(1)	60.782(17)
Sb-Ru(2)-Ru(3)	61.113(16)
Sb-Ru(2)-Ru(1)	53.714(15)
Ru(3)-Ru(2)-Ru(1)	60.447(17)
Sb-Ru(2)-Ru(5)	54.943(14)
Ru(3)-Ru(2)-Ru(5)	63.613(16)
Ru(1)-Ru(2)-Ru(5)	103.196(19)
Sb-Ru(2)-Ru(4)	59.030(15)
Ru(3)-Ru(2)-Ru(4)	110.87(2)
Ru(1)-Ru(2)-Ru(4)	104.498(18)
Ru(5)-Ru(2)-Ru(4)	55.381(14)
Sb-Ru(6)-Ru(4)	63.826(16)
Sb-Ru(6)-Ru(5)	57.616(14)
Ru(4)-Ru(6)-Ru(5)	58.953(15)
Sb-Ru(5)-Ru(4)	62.401(15)
Sb-Ru(5)-Ru(6)	53.175(14)
Ru(4)-Ru(5)-Ru(6)	59.241(15)
Sb-Ru(5)-Ru(2)	54.968(14)
Ru(4)-Ru(5)-Ru(2)	63.174(16)
Ru(6)-Ru(5)-Ru(2)	101.484(17)
Ru(5)-Ru(4)-Sb	55.334(14)
Ru(5)-Ru(4)-Ru(6)	61.806(16)
Sb-Ru(4)-Ru(6)	52.140(15)
Ru(5)-Ru(4)-Ru(2)	61.445(15)
Sb-Ru(4)-Ru(2)	52.751(14)
Ru(6)-Ru(4)-Ru(2)	102.01(2)

3. Molecular and crystal structures.
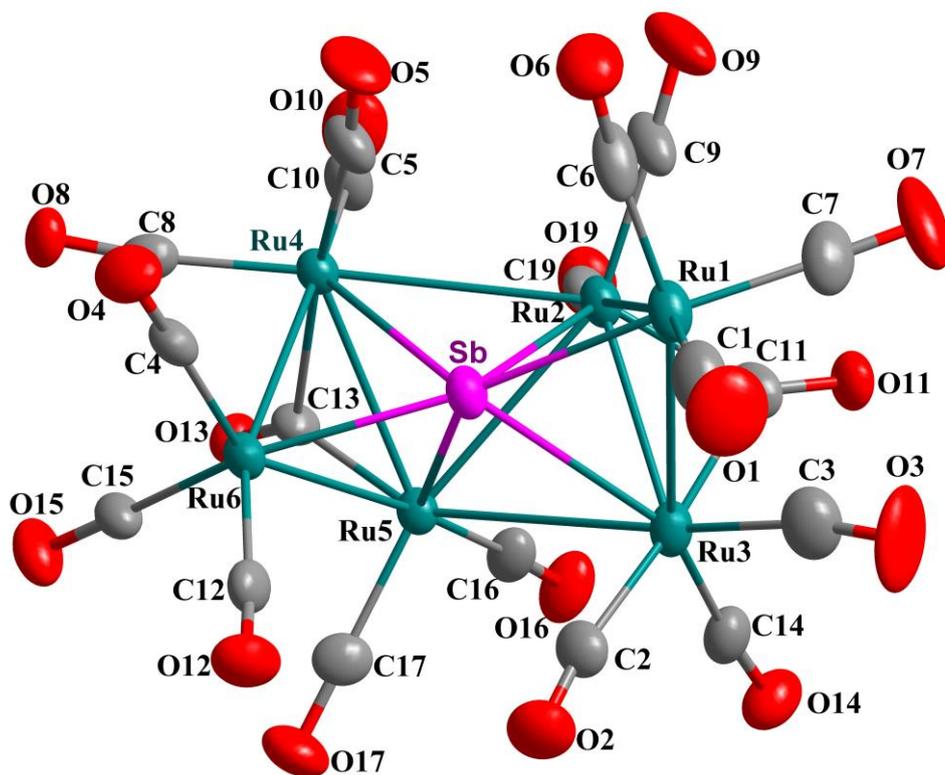
Figure S1.   Atomically labeled structures of [Ru$_6$(μ_6-Sb)(CO)$_{18}$]$^{3-}$ (**1**) with 50% thermal ellipsoids.
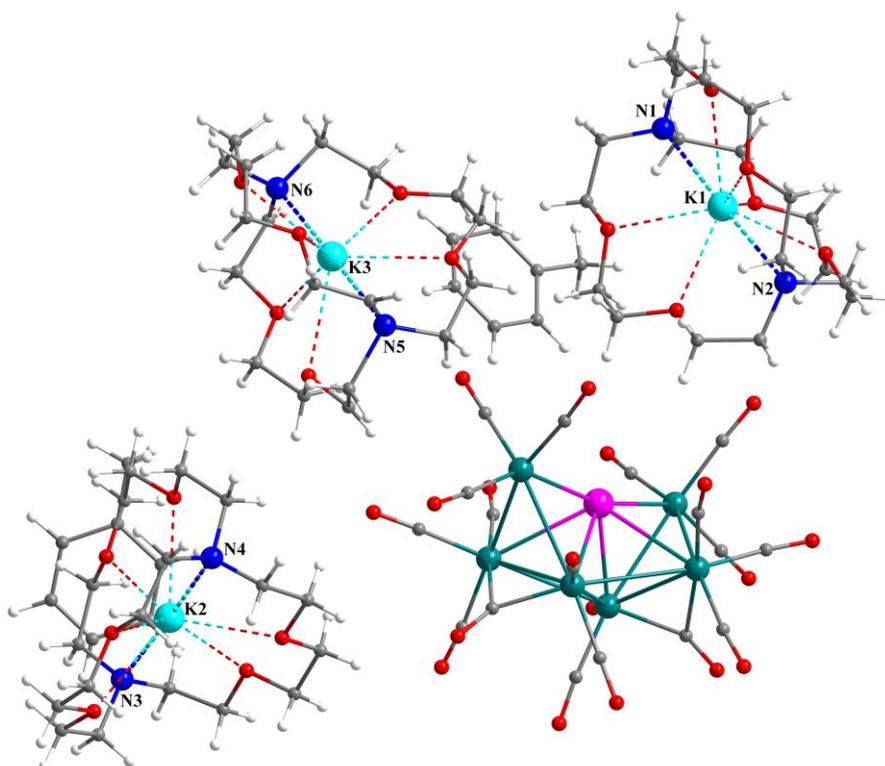

Figure S2.   Structure of [K-2,2,2-cryptand]$_3$·**1**·2tol.
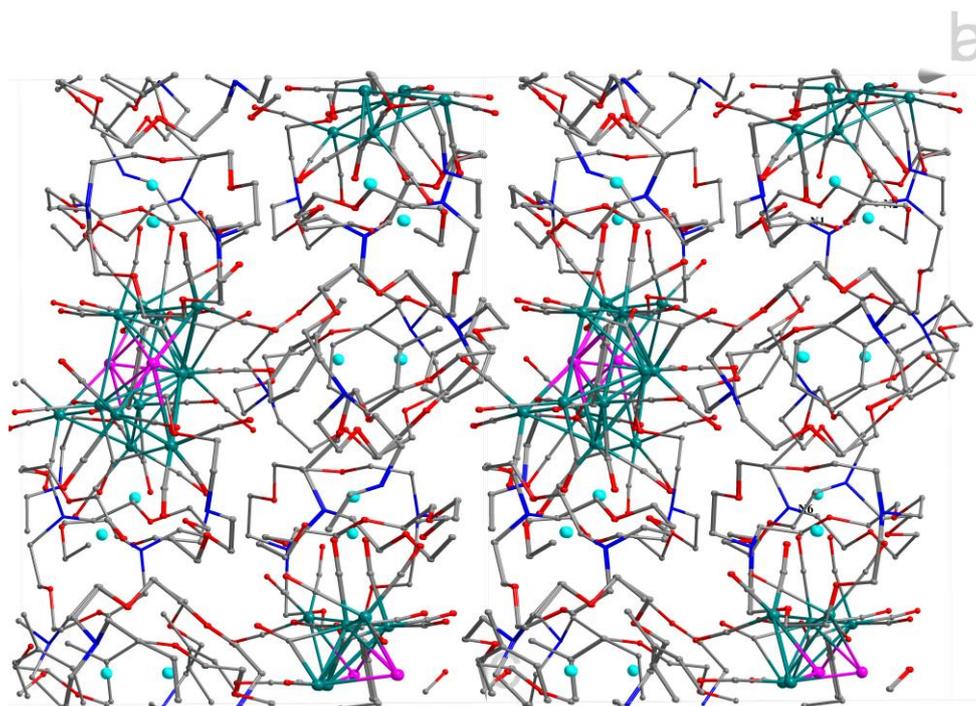
Figure S3. Crystal packing diagram of [K-2,2,2-cryptand]$_3$·**1**·2tol.

4. Spectroscopic characterizations.
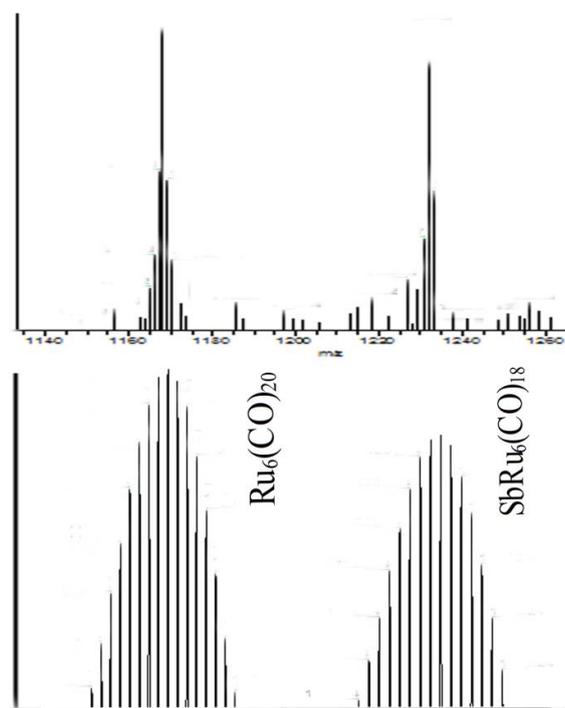
Figure S4. Plus ion-mode electrospray mass spectrum of a DMF solution of [K(2,2,2-cryptand)]$_3$[(μ_6-Sb)Ru$_6$(μ-CO)$_2$(CO)$_{16}$]·2tol.

5. HOMO and LUMO diagrams of 1.
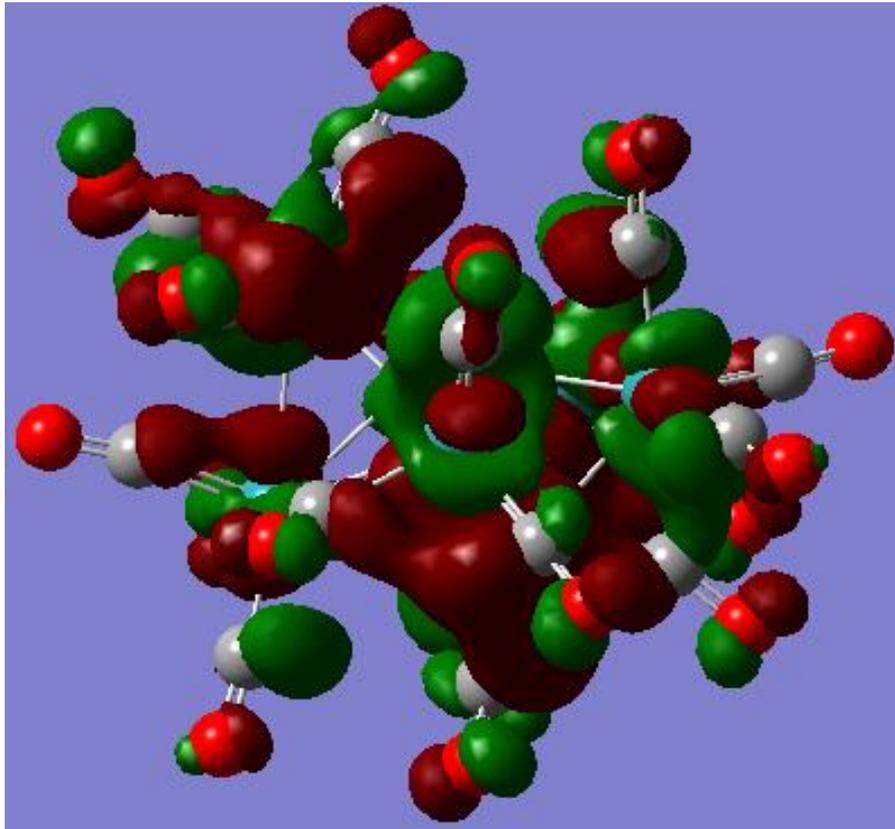
LUMO
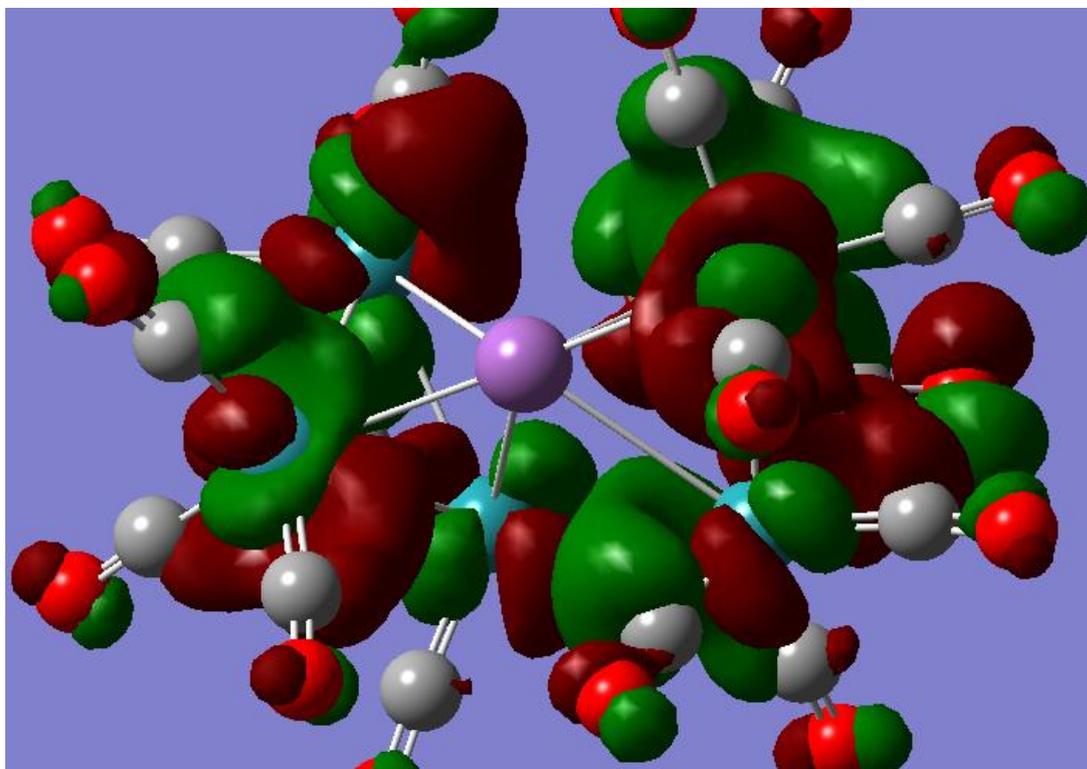
HOMO
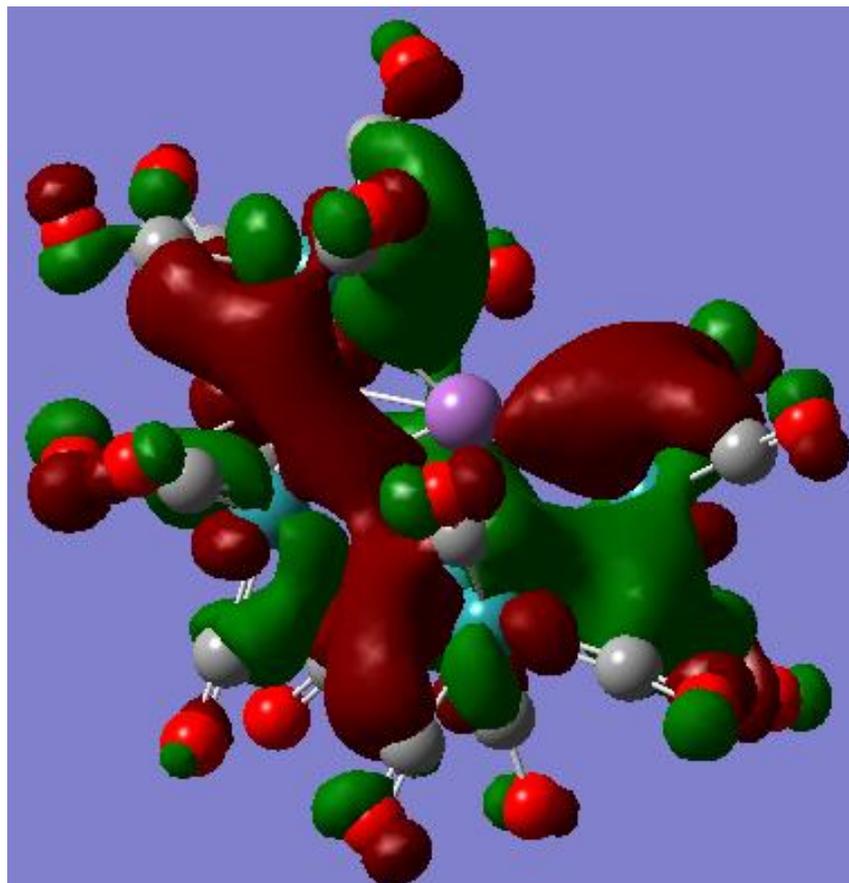
HOMO-1
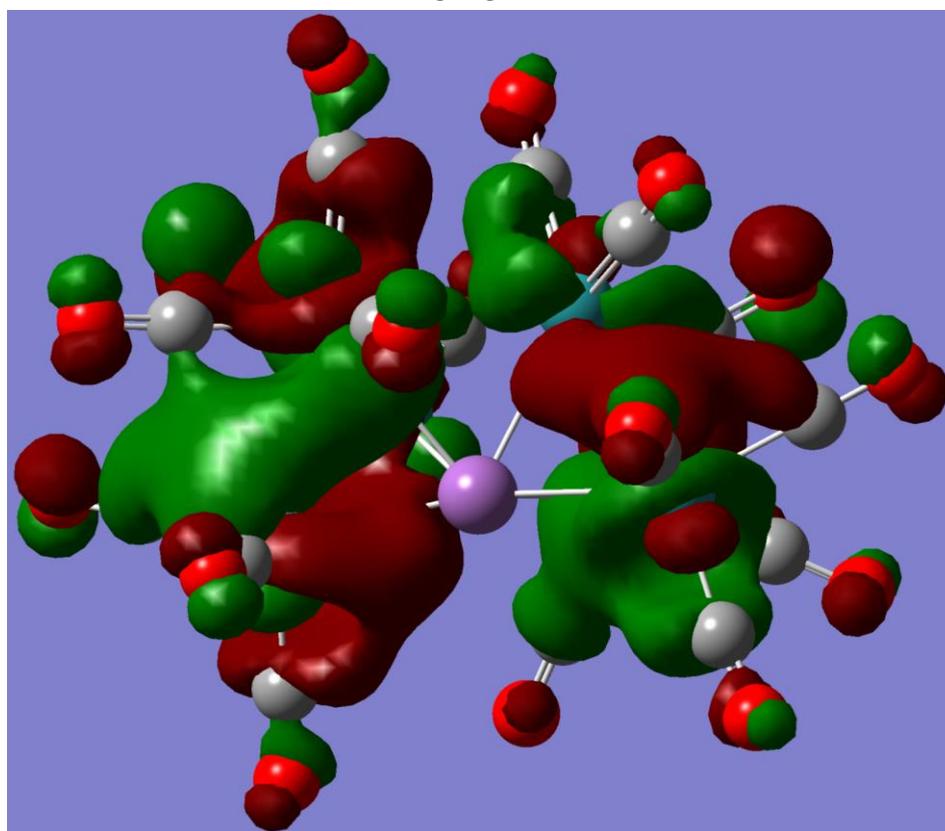
HOMO-2
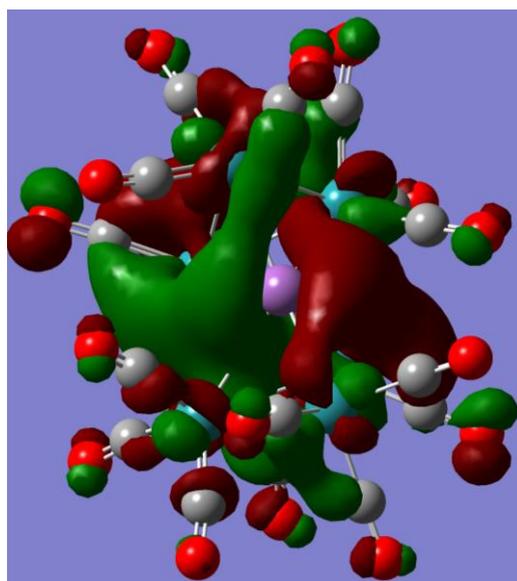
HOMO-3

Figure S5. HOMO/LUMO diagrams of **1**.
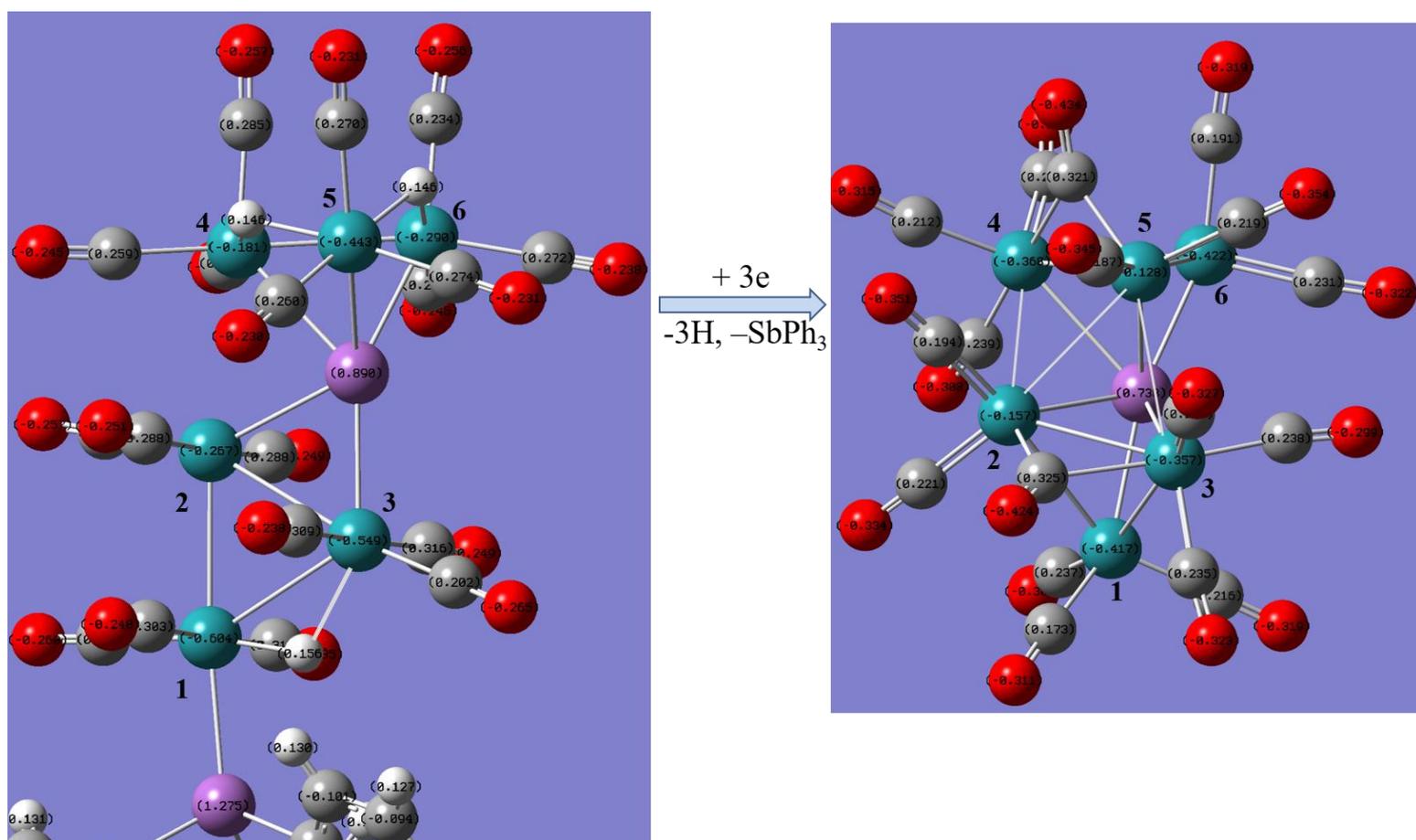

$+ 3e$

$-3H, -SbPh_3$

Figure S6. A comparison of Mulliken atomic charges of **1** and **2**.

Ref. 28. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tmasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford CT, 2009.