Supporting Information

Small Molecules Activation by Mixed Methyl/Methylidene Rare Earth Metal Clusters

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Experimental Section

General Procedures and Materials. All manipulations were performed with rigorous exclusion of air and water, using Schlenk techniques or a Mbraun glovebox (Unilab Mbraun; <1 ppm O_2, <1 ppm H_2O). Toluene, THF and hexane were distilled from sodium strip/benzophenone ketyl, degassed, dried over fresh Na chips and stored in the glovebox. Bis(2,6-Diisopropylphenyl)carbodiimide were obtained from Tokyo Chemical Industry Co., Ltd and used without purification. $CH_3C_6H_4NMe_2$-*o*, *n*BuLi (1.6 mol/L in hexane), PhLi (2.0 mol/L in dibutyl ether) and $AlMe_3$ (1 mol/L in heptane) were purchased from ACROS and used without purification. Phenylacetylene and TMSC≡CH were obtained from J & K and dried by 4Å molecular sieve. Benzonitrile was purchased from ACROS and dried by $CaCl_2$. C_6D_6 was obtained from Cambridge Isotope and dried by sodium chips. CS_2 was obtained from ALFA AESAR and dried by CaH_2. $LnCl_3$[1] and $[(NCN^{dipp})Ln(CH_2C_6H_4NMe_2\text{-}o)_2]$ (Ln = Er, Y, Lu)[2] were prepared according to literature procedure. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL ECA-400 NMR spectrometer (FT, 400 MHz for ^1H; 100 MHz for ^{13}C) in C_6D_6 at room temperature.

Characterization of complexes 2-5.

1. NMR spectra of representative complexes

The solid samples were dissolved in C_6D_6, and then transferred into a J-Young NMR tube in the glove-box. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL ECA-400 NMR spectrometer (FT, 400 MHz for ^1H; 100 MHz for ^{13}C) in C_6D_6 at room temperature.

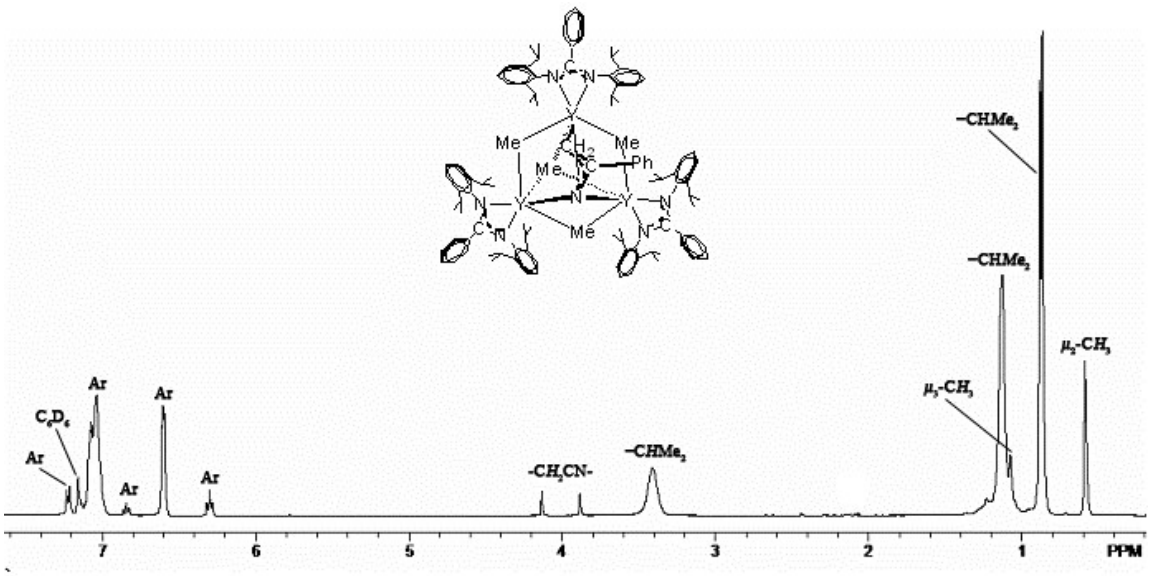

Figure S1. ^{1}H NMR spectrum of **2a** obtained in C_6D_6 at room temperature.

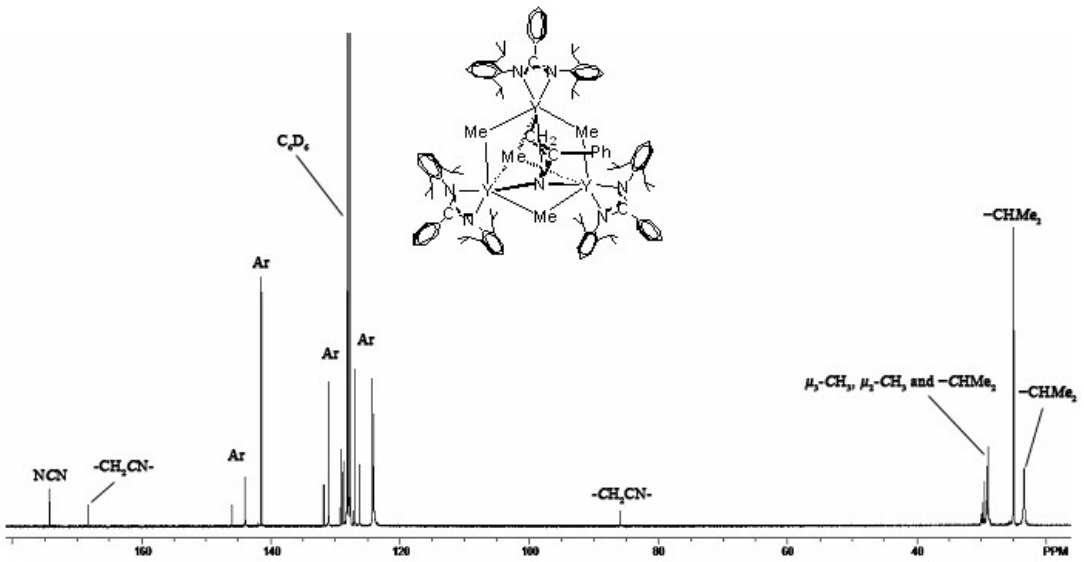

Figure S2. ^{13}C NMR spectrum of **2a** obtained in C_6D_6 at room temperature.

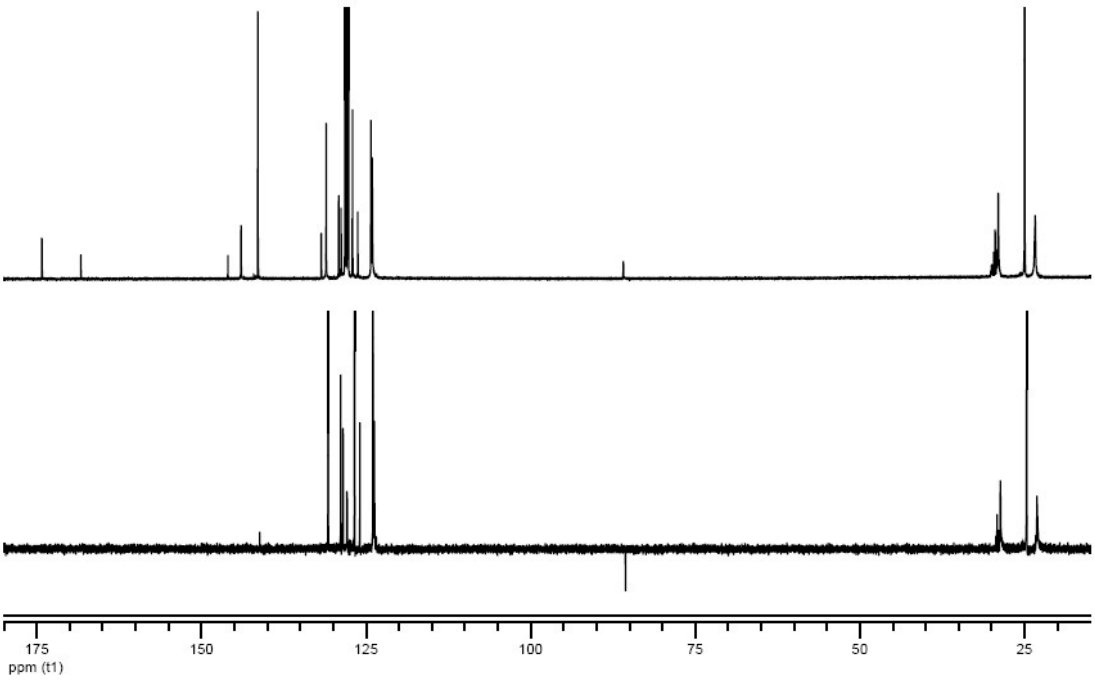

Figure S3. ^{13}C and ^{13}C DEPT-135 spectrum of complex **2a**.

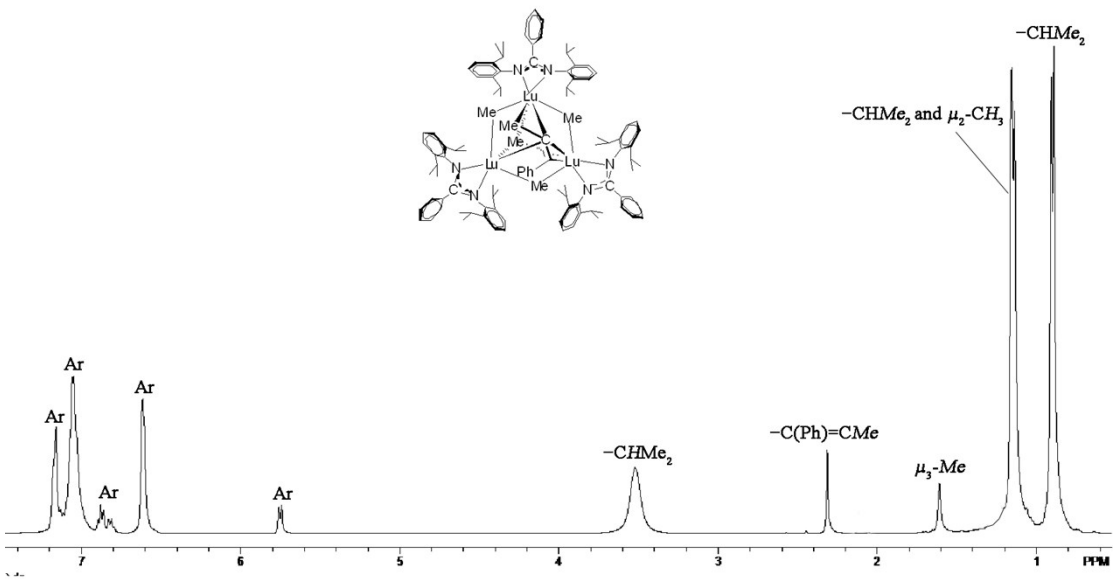

Figure S4. ^{1}H NMR spectrum of **3b** obtained in C_6D_6 at room temperature.

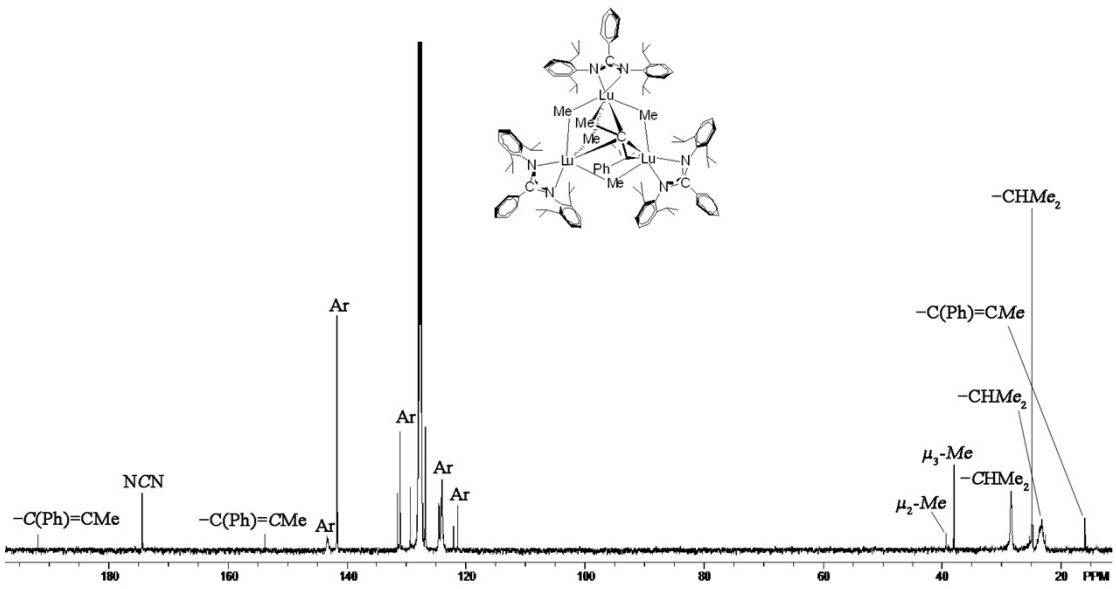

Figure S5. ^{13}C NMR spectrum of **3b** obtained in C_6D_6 at room temperature.

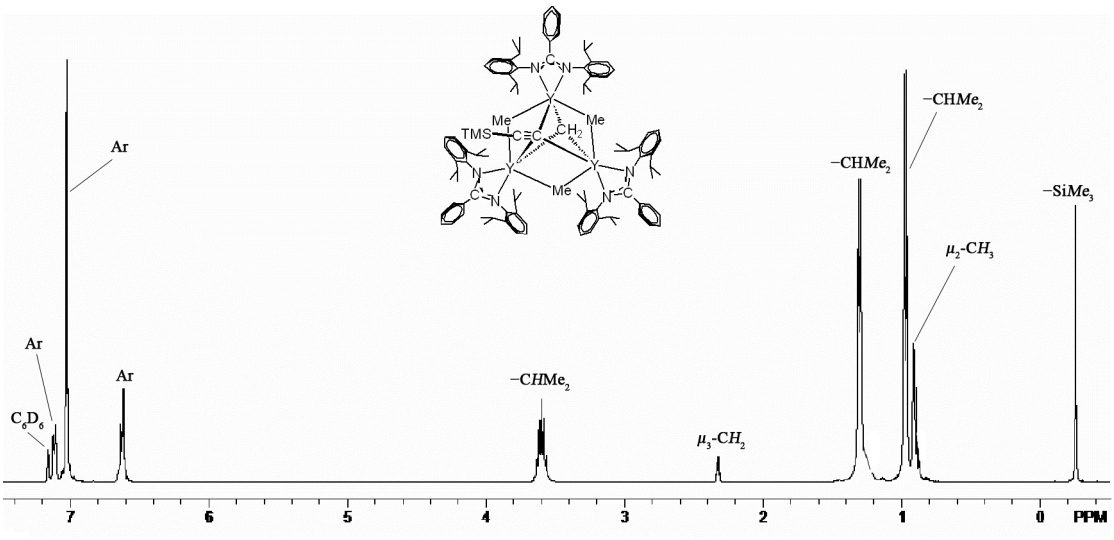

Figure S6. ^{1}H NMR spectrum of **4a** obtained in C_6D_6 at room temperature.

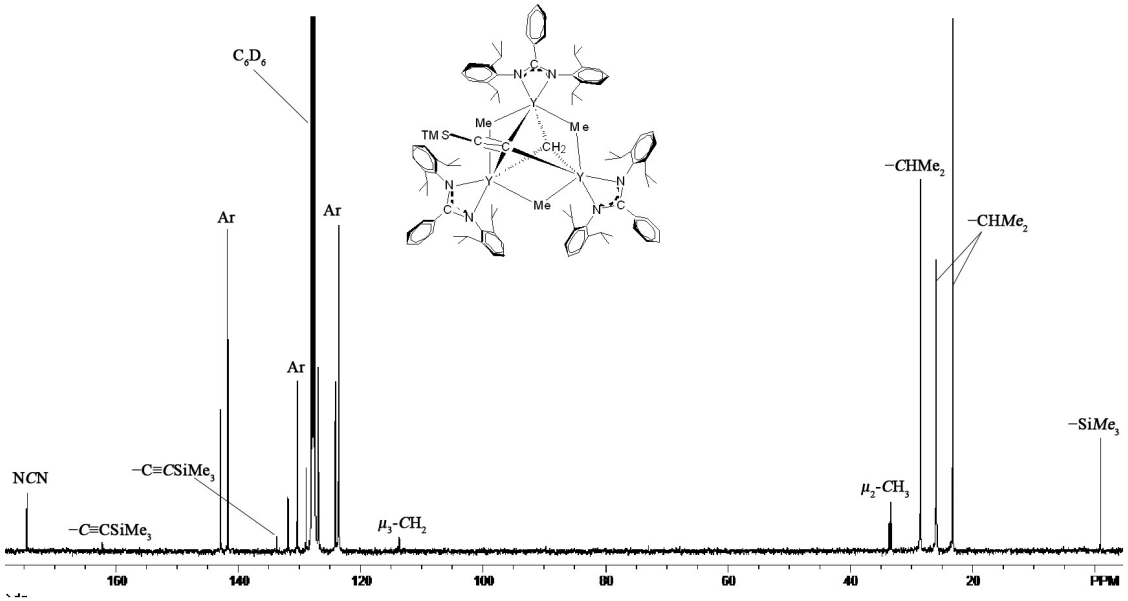

Figure S7. ^{13}C NMR spectrum of **4a** obtained in C_6D_6 at room temperature.

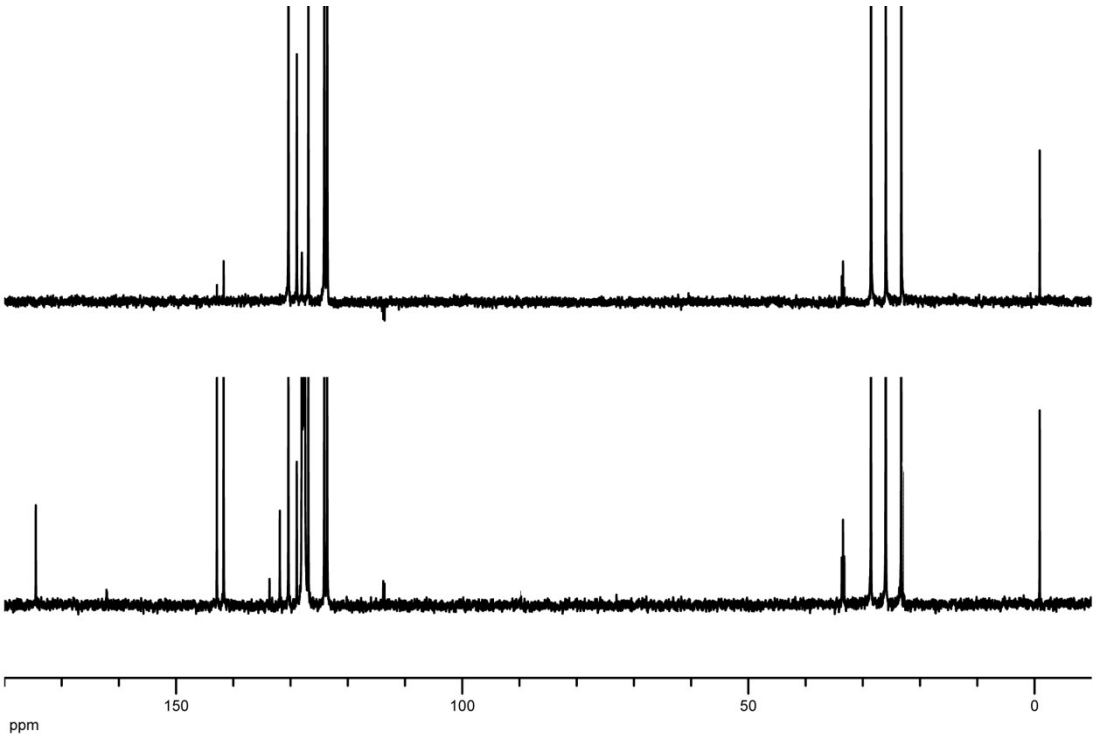

Figure S8. ^{13}C DEPT-135 and ^{13}C spectrum of complex **4a**.

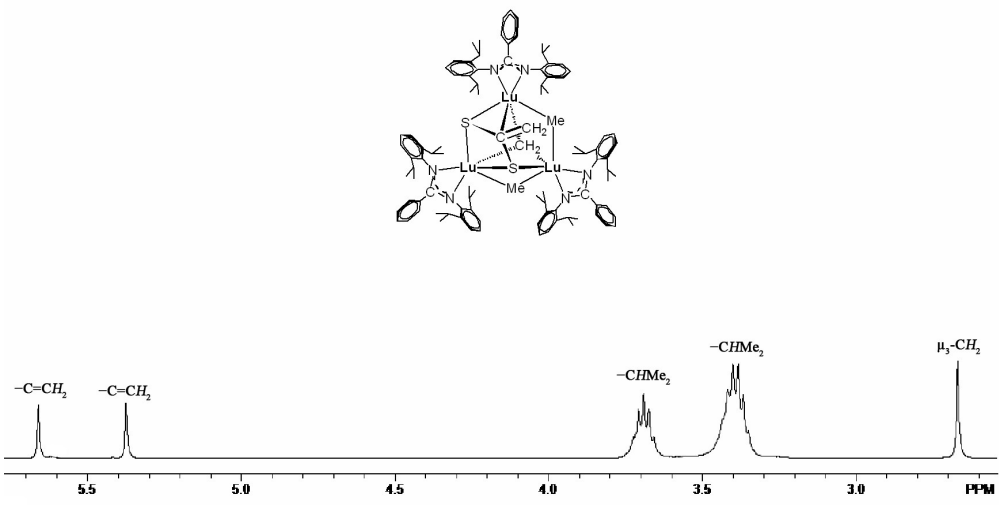

Figure S9. ^{1}H NMR spectrum of **5b**: resonance of −C=CH_2, −CHMe$_2$ and μ_3-CH_2 protons

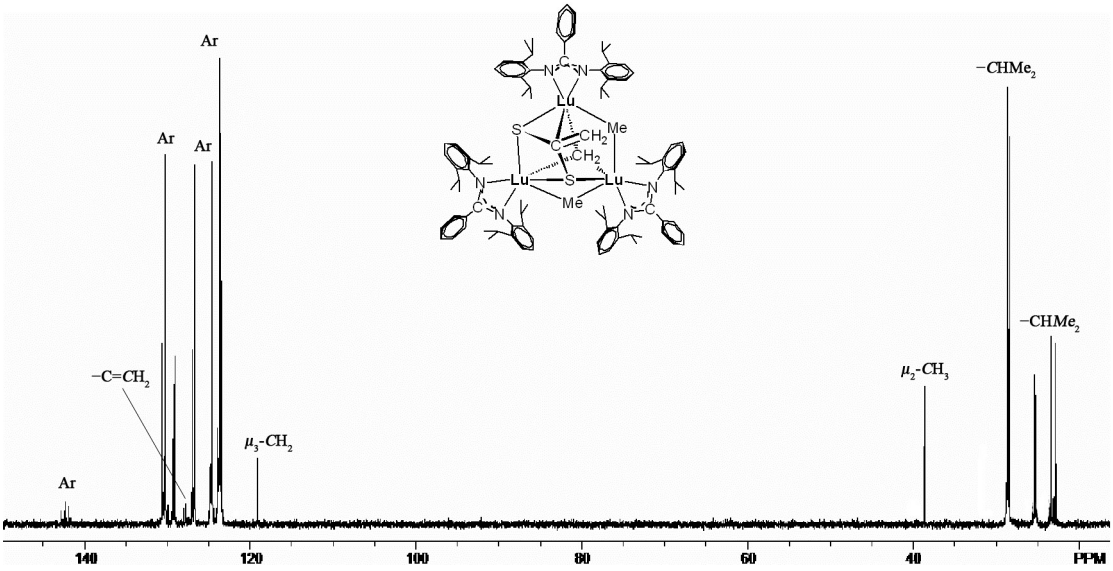

Figure S10. ^{13}C DEPT-45 spectrum of **5b** obtained in C_6D_6 at room temperature.

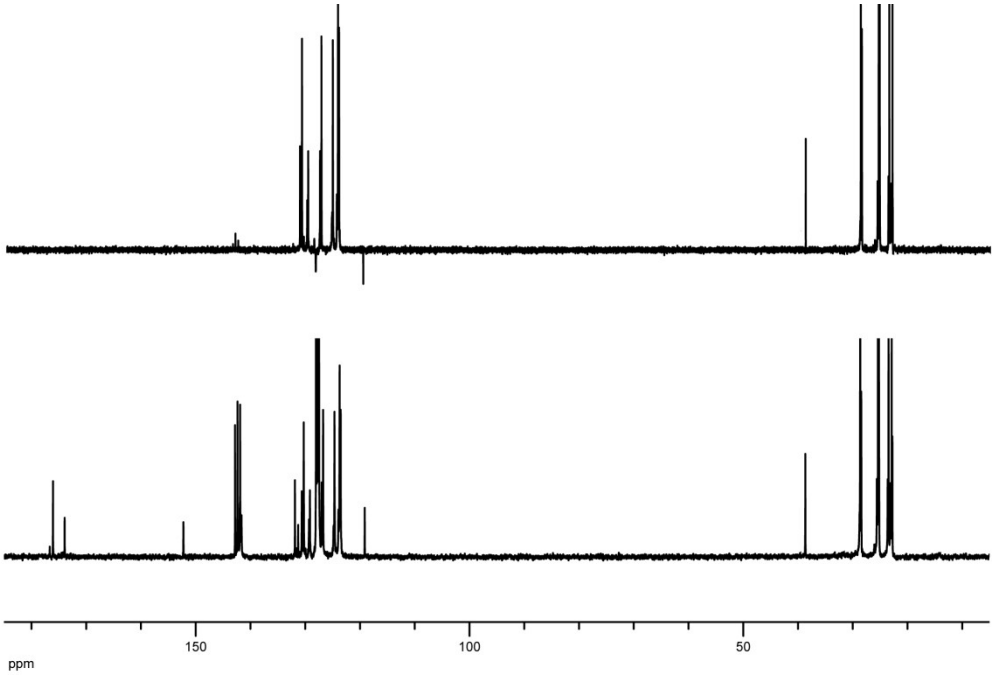

Figure S11. ^{13}C DEPT-135 and ^{13}C spectrum of complex **5b**.

X-ray Crystallographic Analysis. Suitable crystals were sealed in the thin-wall glass capillaries under a microscope in the glove box. Data collections were performed on a Bruker SMART APEX diffractometer with CCD area detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The determination of crystal class and unit cell was carried out by SMART program package. The raw frame data were processed using SAINT[3] and SADABS[4] to yield the reflection data file. The structure was solved by using SHELXTL program[5]. Refinement was performed on F^2 anisotropically by the full-matrix least-squares method for all the non-hydrogen atoms. The analytical scattering factors for neutral atoms were used throughout the analysis. Except for the hydrogen atoms on bridging-carbons, hydrogen atoms were placed at the calculated positions and included in the structure calculation without further refinement of the parameters. The hydrogen atoms on bridging-carbons were located by difference Fourier syntheses and their coordinates and isotropic parameters were refined. The residual electron densities were of no chemical significance. CCDC 1405778 (complex **1c**), 845812 (complex **2a**), 845817 (complex **3b**), 845815 (complex **4a**) and 845816 (complex **5b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44)-1223-336033; or deposit@ccdc.cam.ac.uk).

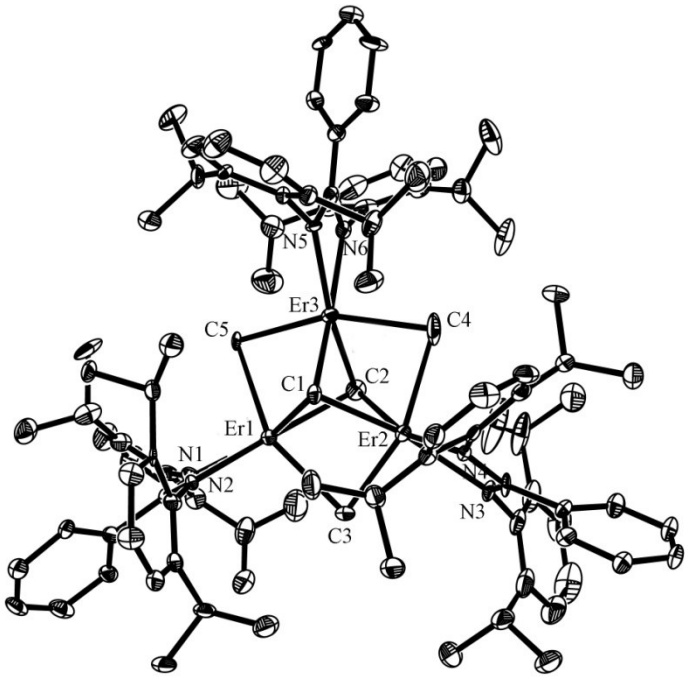

Figure S12. Molecular structure of **1c** (thermal ellipsoids at 30% level; solvent molecules and hydrogen atoms are omitted for clarity).

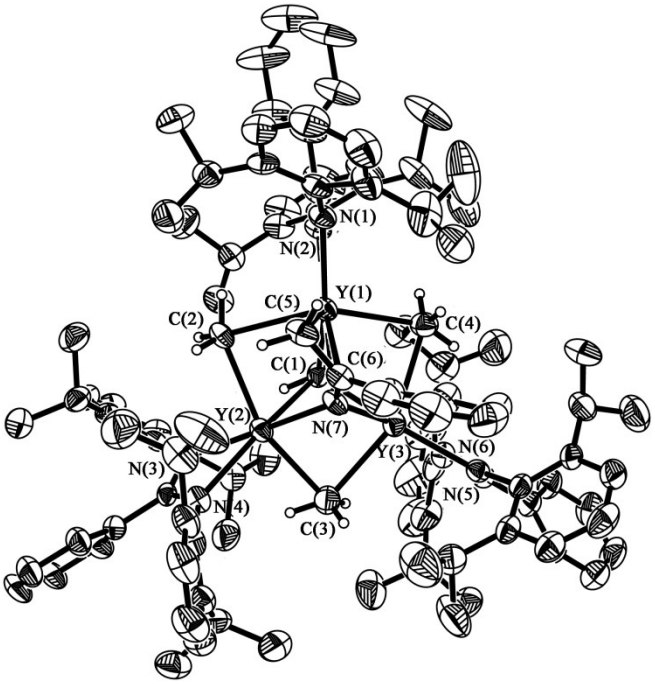

Figure S13. Molecular structure of **2a** (thermal ellipsoids at 30% level; solvent molecules and parts of hydrogen atoms are omitted for clarity).

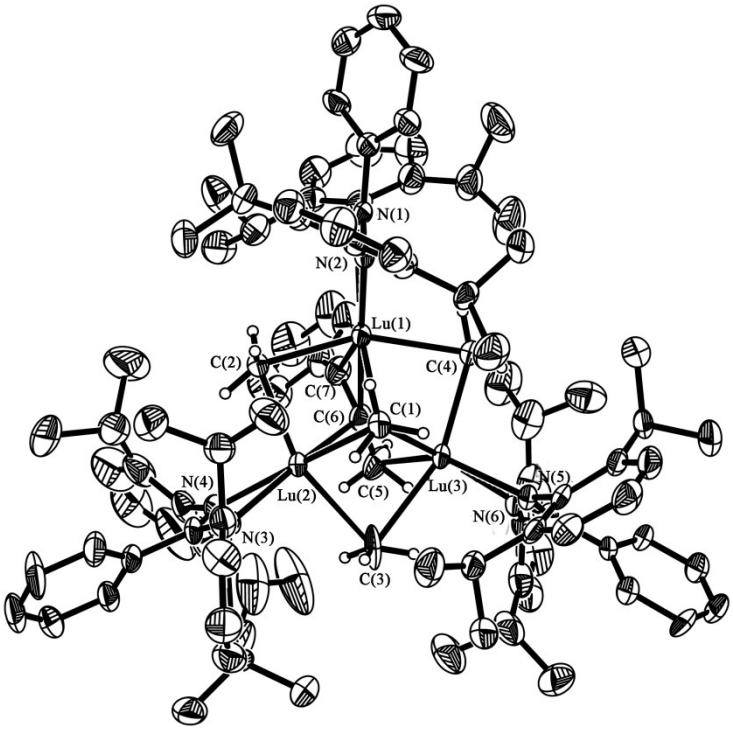

Figure S14. Molecular structure of **3b** (thermal ellipsoids at 30% level; solvent molecules and parts of hydrogen atoms are omitted for clarity).

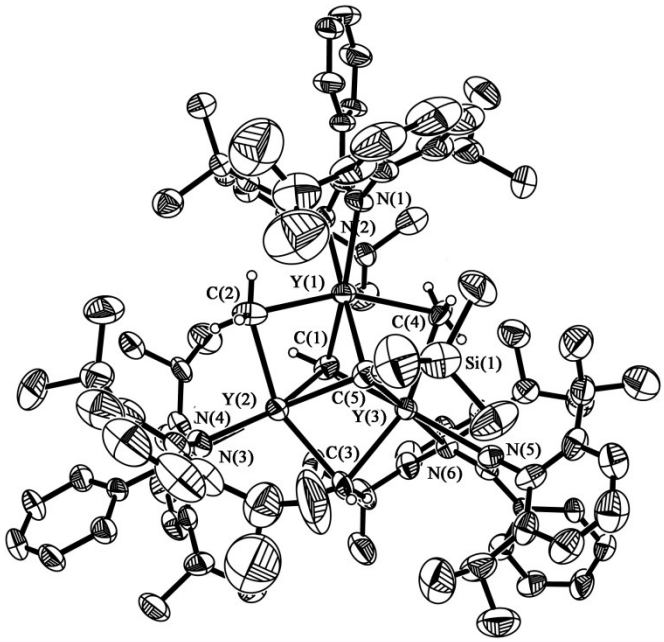

Figure S15. Molecular structure of **4a** (thermal ellipsoids at 30% level; solvent molecules and parts of hydrogen atoms are omitted for clarity).

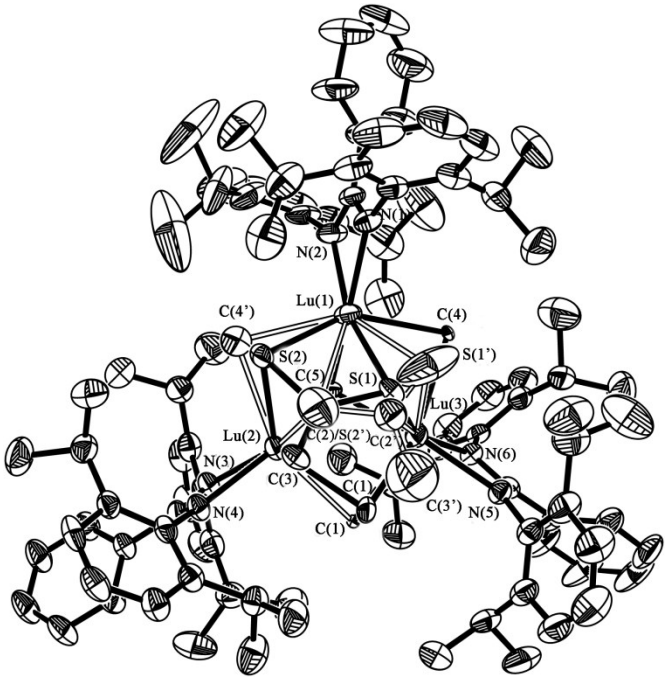

Figure S16. Molecular structure of **5b** (thermal ellipsoids at 30% level; solvent molecules and hydrogen atoms are omitted for clarity).

References

1. R. W. Stotz, G. A. Melson, *Inorg. Chem.*, 1972, **11**, 1720-1721.

2. (a) L. Zhang, M. Nishiura, M. Yuki, Y. Luo, Z. Hou, *Angew. Chem. Int. Ed.*, 2008, **47**, 2642 –2645; (b) M. Nishiura, Z. Hou, *Nat. Chem.*, 2010, **2**, 257-268.

3. *SAINTPlus Data Reduction and Correction Program* v. 6.02 a; Bruker AXS: Madison, WI, 2000.

4. Sheldrick, G. M. *SADABS*, A Program for Empirical Absorption Correction; University of Göttingen: Göttingen, Germany, 1998.

5. Sheldrick, G. M. *SHELXL-97*, Program for the Refinement of Crystal Structures; University of Göttingen: Göttingen, Germany, 1997.