



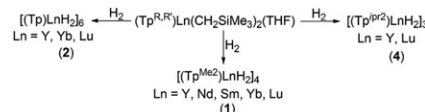
## Contents

### REVIEW ARTICLE

**Jianhua Cheng, Kuburat Saliu,  
Michael J. Ferguson, Robert McDonald,  
Josef Takats**

*J. Organomet. Chem.* 695 (2010) 2696

Lanthanide polyhydrides of different sizes have been obtained by hydrogenolysis of various scorpionate anchored lanthanide dialkyl complexes,  $(\text{Tp}^{\text{R,R'}})\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})$ . The nuclearity of the cluster hydrides can be controlled by judicious choice of the scorpionate ligand. The solid-state structures of the currently available  $[(\text{Tp}^{\text{R,R'}})\text{LnH}_2]_n$  complexes are reviewed.

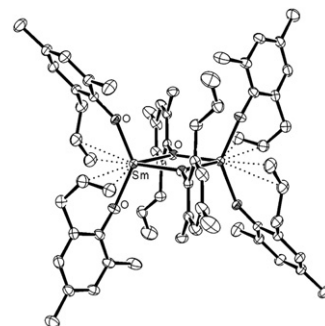


### SYNTHESIS AND STRUCTURE OF ORGANOLANTHANIDE COMPOUNDS

**David J. Berg, Tosha Barclay, Xuening Fei**

*J. Organomet. Chem.* 695 (2010) 2703

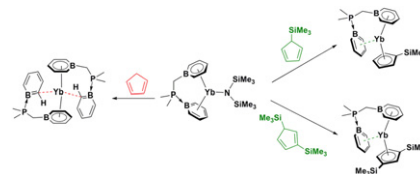
Aryloxides bearing *ortho*-allyl substituents form the first neutral, trivalent lanthanide complexes containing metal–alkene bonds in both the solid state and solution.



**Peng Cui, Yaofeng Chen, Qiang Zhang,  
Guangyu Li, Wei Xia**

*J. Organomet. Chem.* 695 (2010) 2713

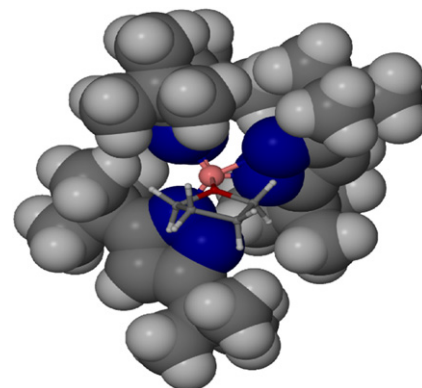
The preparation and characterization of the solvent-free divalent ytterbium bis(boratabenzene) complex  $[\text{C}_5\text{H}_5\text{BCH}_2(\text{CH}_3)_2\text{P} \rightarrow \text{BC}_5\text{H}_5]_2\text{Yb}$  (**2a**) and heteroleptic complexes  $[\text{C}_5\text{H}_3\text{R}^1\text{R}^2][\text{C}_5\text{H}_5\text{BCH}_2(\text{CH}_3)_2\text{P} \rightarrow \text{BC}_5\text{H}_5]\text{Yb}$  (**3**;  $\text{R}^1 = \text{SiMe}_3$ ,  $\text{R}^2 = \text{H}$ ; **4**:  $\text{R}^1 = \text{R}^2 = \text{SiMe}_3$ ) are reported. The interactions between the pendant neutral borabenzene and the ytterbium center were observed both in the solid-state and in benzene solution. Addition of external  $\sigma$ -donor solvent THF to the complexes caused a dissociation of the neutral borabenzene from the ytterbium center.



**Jacinta M. Bakker, Leonard J. Barbour,  
Glen B. Deacon, Peter C. Junk, Gareth  
O. Lloyd, Jonathan W. Steed**

*J. Organomet. Chem.* 695 (2010) 2720

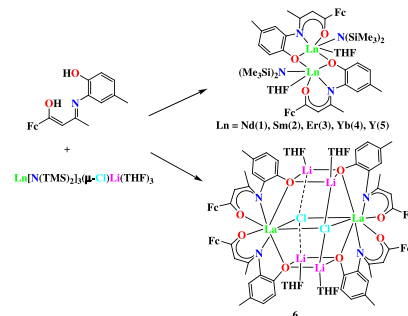
Aluminum complexes with 3,5-*t*-butylpyrazolate ligands are synthesised from aluminium metal and  $\text{Hg}(\text{C}_6\text{F}_5)_2$  using the Redox transmetalation/ligand exchange reaction. The results contain insights into the chemistry of these reactions and the solvent coordination possibilities of the products. Crystallographic insights into the structures are also presented.



**Xiang-Yong Gu, Xiang-Zong Han, Ying-Ming Yao, Yong Zhang, Qi Shen**

*J. Organomet. Chem.* 695 (2010) 2726

A series of organolanthanide complexes supported by a new ferrocene-containing N-aryloxo-functionalized  $\beta$ -ketoiminate ligand was synthesized by amine elimination reactions, and it was found that the ionic radii have a profound effect on the outcome of the reactions.

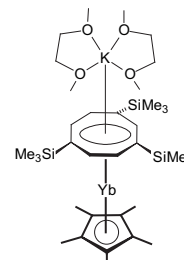


**Anja Edelmann, Cristian G. Hrib,  
Steffen Blaurock, Frank T. Edelmann**

*J. Organomet. Chem.* 695 (2010) 2732

The influence of bulky silyl-substituted cyclooctatetraenyl ligands on the formation and structure of ytterbium sandwich complexes has been investigated. The reaction of  $\text{YbCl}_3$  with  $[\text{K}(\text{DME})]_2(\text{COT}^{\text{TBS}})$  (**2**,  $\text{COT}^{\text{TBS}} = [\text{C}_8\text{H}_6(\text{SiMe}_2^t\text{Bu})_{2-1,4}]^{2-}$ ) and  $\text{KCp}^*$

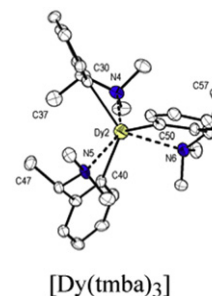
( $\text{Cp}^* = \text{pentamethylcyclopentadienyl}$ ) in DME solution afforded a mixture of neutral  $\text{Cp}^*\text{Yb}(\text{COT}^{\text{TBS}})$  (**3**, purple crystals) and anionic  $[\text{K}(\text{DME})_4][\text{Yb}(\text{COT}^{\text{TBS}})_2]$  (**4**, royal blue crystals). In contrast, the closely related reaction of  $\text{YbCl}_3$  with  $\text{K}_2(\text{DME})_2(\text{COT}^{\text{'''}})$  (**5**,  $\text{COT}^{\text{'''}} = [\text{C}_8\text{H}_5(\text{SiMe}_3)_3-1,3,6]^{2-}$ ) and  $\text{KCp}^*$  resulted in spontaneous reduction of  $\text{Yb}^{3+}$  to the divalent oxidation state and formation of dark blue-green  $(\text{DME})_2\text{K}(\mu\text{-COT}^{\text{'''}})\text{-YbCp}^*$  (**6**) as the sole reaction product. The compounds **3**, **4**, and **6** were structurally characterized by X-ray diffraction.



**Alex R. Petrov, Oliver Thomas,  
Klaus Harms, Konstantin A. Rufanov,  
Jörg Sundermeyer**

*J. Organomet. Chem.* 695 (2010) 2738

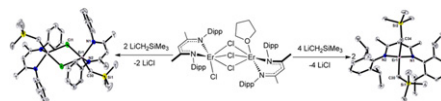
Stabilization of homoleptic *tris*-aryl rare-earth metal complexes (Y, Sm, Dy, Nd, Lu) was achieved when benzylic  $\text{CH}_2$  protons in *ortho*-metallated dimethylbenzylamine (dmba) are substituted by one or two methyl groups (tmba, cuda ligands).



**Kevin R.D. Johnson, Adrien P. Côté,  
Paul G. Hayes**

*J. Organomet. Chem.* 695 (2010) 2747

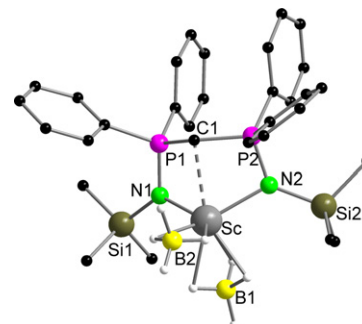
The synthesis and reactivity of a novel series of organoerbium complexes supported by a  $\beta$ -diketiminato ancillary ligand are described. All complexes, including a rare 4-coordinate dialkyl species, have been characterized by X-ray crystallography.



**Jelena Jenter, Georg Eickerling,  
Peter W. Roesky**

*J. Organomet. Chem.* 695 (2010) 2756

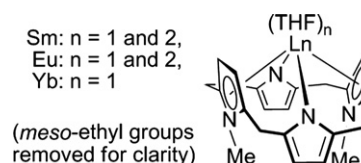
Bis(phosphinimino)methanide rare earth metal bis(borohydrides)  $[(\text{Me}_3\text{SiNPPh}_2)_2\text{CH}]\text{-Nd}(\text{BH}_4)_2(\text{THF})$  and  $[(\text{Me}_3\text{SiNPPh}_2)_2\text{CH}]\text{Sc}(\text{BH}_4)_2$  were prepared by reaction of  $[\text{Ln}(\text{BH}_4)_3(\text{THF})_n]$  and  $\text{K}\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}$ .



**Andrew K.J. Dick, Alistair S.P. Frey,  
Michael G. Gardiner, Matthias Hilder,  
Adam N. James, Peter C. Junk,  
Suraphan Powanosorn, Brian W.  
Skelton, Jun Wang, Allan H. White**

*J. Organomet. Chem.* 695 (2010) 2761

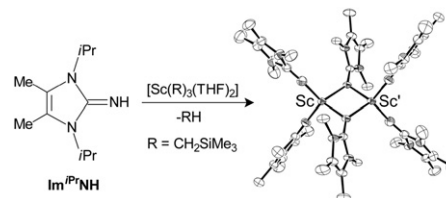
Sm(II), Eu(II) and Yb(II) complexes of doubly deprotonated *trans*-*N,N'*-dimethyl-*meso*-octaethylporphyrinogen were synthesised as tetrahydrofuran adducts (Sm and Eu, bis; Yb, mono) by metathetical exchange reactions. The Sm and Eu complexes partially desolvate in non-coordinating solvents to give mono-tetrahydrofuran adducts. Reactions with 1,4-di-*t*-butyl-1,4-diazabuta-1,3-diene have been explored.



**Tarun K. Panda, Cristian G. Hrib,  
Peter G. Jones, Matthias Tamm**

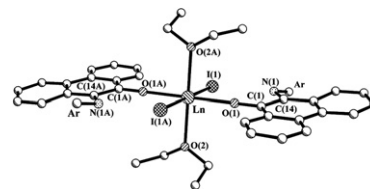
*J. Organomet. Chem.* 695 (2010) 2768

Homoleptic tris(imidazolin-2-iminato) rare earth metal complexes are obtained from the reactions of the imines  $\text{Im}^{\text{iPr}}\text{NH}$  and  $\text{Im}^{\text{tBu}}\text{NH}$  with trimethylsilylmethyl (neosilyl) complexes  $[\text{M}(\text{CH}_2\text{SiMe}_3)(\text{THF})_2]$  ( $\text{M} = \text{Sc}, \text{Y}, \text{Lu}$ ). The  $\text{Im}^{\text{iPr}}\text{N}$  ligand affords dinuclear species of the type  $[\text{M}_2(\text{Im}^{\text{iPr}}\text{N})_6(\text{THF})_n]$  ( $n = 0, \text{M} = \text{Sc}$ ;  $n = 1, \text{M} = \text{Y}, \text{Lu}$ ), whereas the more sterically demanding  $\text{Im}^{\text{tBu}}\text{N}$  ligand produces the mononuclear complex  $[\text{Y}(\text{Im}^{\text{tBu}}\text{N})_3(\text{THF})_2]$ .



Mikhail N. Bochkarev, Anatoly A. Fagin,  
Nikolai O. Druzhkov, Vladimir  
K. Cherkasov, Marina A. Katkova, Georgy  
K. Fukin, Yurii A. Kurskii

*J. Organomet. Chem.* 695 (2010) 2774

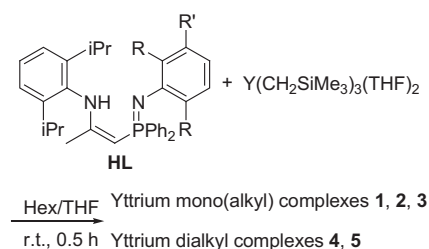


### CATALYSIS WITH ORGANOLANTHANIDE COMPOUNDS

Danfeng Li, Shihui Li, Dongmei Cui,  
Xuequan Zhang

*J. Organomet. Chem.* 695 (2010) 2781

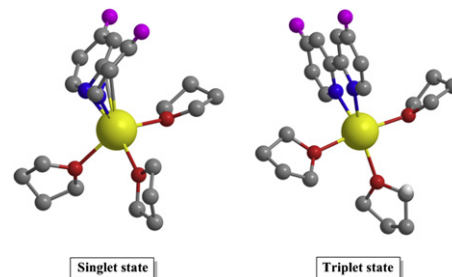
The reactions between  $HL^{1-3}$  and  $Y(CH_2SiMe_3)_3(THF)_2$  generated mono(alkyl) complexes **1**, **2**, and **3** via deprotonation and C–H bond activation. However, when compounds  $HL^{4,5}$  were used, the dialkyl complexes **4** and **5** were formed by deprotonation. The activation position correlated with the steric bulkiness of aryl substituents of phosphinimino moiety.



Ahmed Yahia, Mathias U. Kramer,  
Jun Okuda, Laurent Maron

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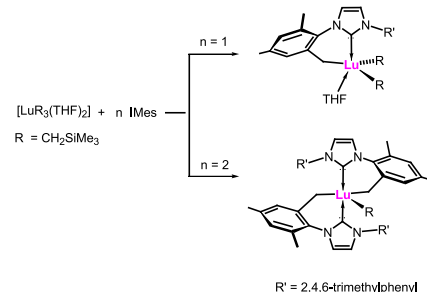
Applying DFT methods, the reductive elimination reaction of bis(pyridyl) rare-earth metal cation  $[Ln(\eta^2-C,N\text{-pyridyl})_2(THF)_3]^+$  ( $Ln = Y, La$ ) was studied. An alternative mechanism for the C–C coupling reaction between pyridine ligands is suggested. The reaction involves a single electron reductive C–C coupling to form of Ln(II) complexes with bipyridine radical anions.



Waldemar Fegler, Teruhiko Saito,  
Kazushi Mashima, Thomas P. Spaniol,  
Jun Okuda

*J. Organomet. Chem.* 695 (2010) 2794

The N-heterocyclic carbene bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) reacted with the tris(trimethylsilylmethyl) complex  $[Ln(CH_2SiMe_3)_3(THF)_2]$  to give a  $C_2$ -symmetric mono(trimethylsilylmethyl) complex  $[Ln(CH_2SiMe_3)(IMes)_2]$  as well as a mono-activated product  $[Ln(CH_2SiMe_3)_2(IMes')(THF)_n]$ .

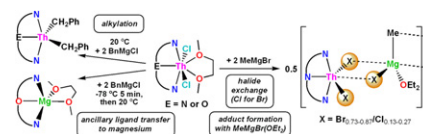


## ORGANOACTINIDE COMPOUNDS

**Carlos A. Cruz, Terry Chu, David J.H. Emslie, Hilary A. Jenkins, Laura E. Harrington, James F. Britten**

*J. Organomet. Chem.* 695 (2010) 2798

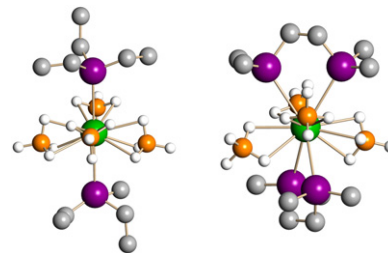
A diversity of products was obtained in the reactions of alkyl Grignard reagents with NNN- and NON-donor ligated thorium(IV) chloride complexes. With MeMgBr, halide exchange and adduct formation yielded tetrametallic  $[\{LThX(\mu-X)_2Mg(OEt_2)(\mu-Me)\}_2]$  ( $X = Br_{0.73-0.87}/Cl_{0.13-0.27}$ ). By contrast, with PhCH<sub>2</sub>MgCl, alkylation and/or ligand transfer to magnesium was observed, depending on the conditions.



**Andrew C. Dunbar, John E. Gozum, Gregory S. Girolami**

*J. Organomet. Chem.* 695 (2010) 2804

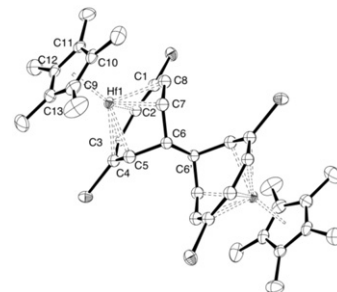
Three phosphine complexes of thorium(IV) borohydride have been prepared – Th(BH<sub>4</sub>)<sub>4</sub>(PMe<sub>3</sub>)<sub>2</sub>, Th(BH<sub>4</sub>)<sub>4</sub>(PEt<sub>3</sub>)<sub>2</sub>, and Th(BH<sub>4</sub>)<sub>4</sub>(dmpe)<sub>2</sub>, where dmpe = 1,2-bis-(dimethylphosphino)ethane, of which two have been structurally characterized. The results include the first thorium complex of a unidentate phosphine, and the first thorium complex of a bidentate borohydride ligand.



**Z.E. Button, F.G.N. Cloke, N.A. Morley-Smith, M.P. Coles, P.B. Hitchcock**

*J. Organomet. Chem.* 695 (2010) 2809

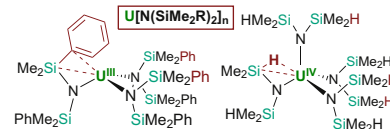
Reduction of  $[Zr(\eta-COT\{Si^iPr_3-1,4\}_2)(\eta-Cp^*)-Cl]$  with K<sub>C<sub>8</sub></sub> in toluene affords the monomeric Zr(III) mixed-sandwich complex  $[Zr(\eta-COT\{Si^iPr_3-1,4\}_2)(\eta-Cp^*)]$ , whereas the analogous reaction of the hafnium complex  $[Hf(\eta-COT\{Si^iPr_3-1,4\}_2)(\eta-Cp^*)]$  results in coupling of the COT rings to give dimeric  $[Hf(\eta-Cp^*)]_2(\mu-\eta^7, \eta^7-(C_8H_6\{Si^iPr_3-3,6\}_2)C_8H_6\{Si^iPr_3-3,6\}_2)]$ .



**Stephen M. Mansell, Bernabé Fernández Perandones, Polly L. Arnold**

*J. Organomet. Chem.* 695 (2010) 2814

The deprotonation of bulky amides such as HN(SiMe<sub>2</sub>Ph)<sub>2</sub> may be accelerated by the use of catalytic quantities of an alkali metal *tert*-butoxide salt. The uranium(IV) and uranium(III) complexes  $[U\{N(SiMe_2H)_2\}_4]$  and  $[U\{N(SiMe_2Ph)_2\}_3]$  are reported; both exhibit weak interactions between uranium silyl-H or silyl-Ph groups in the solid-state.



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**Selma Duhović, Marisa J. Monreal,  
Paula L. Diaconescu**

*J. Organomet. Chem.* 695 (2010) 2822

A uranium benzyl complex supported by a ferrocene-diamide ligand reacts with quinoline by transferring the alkyl ligand to the pyridine ring.

