Group 3 and Group 13 Metal Hydride Compounds

DISSERTATION

zur Erlangung des akademischen Grades eines

Doktors der Naturwissenschaften (Dr. rer. nat.)

im Fach Chemie der Fakultät für Biologie, Chemie und Geowissenschaften

der Universität Bayreuth

vorgelegt von

Dipl. Chem. Tobias Bauer

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The following work has been carried out in the period September 2009 to July 2013 at the Lehrstuhl für Anorganische Chemie II of the Universität Bayreuth under the supervision of Prof. Dr. Rhett Kempe.

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Meiner Familie in Dankbarkeit gewidmet

„Das Außerordentliche geschieht nicht auf glattem, gewöhnlichem Wege."

Johann Wolfgang von Goethe

Alphabetical list of abbreviations

alane	aluminum hydride
Ap	aminopyridinate, aminopyridinato ligand
ApH	aminopyridine
°C	degree celsius
Cp	cyclopentadienyl ligand
ELI-D	electron localizability indicator
Et	ethyl
Gu	guanidinate, guanidinato ligand
GuH	guanidine
NMR	nuclear magnetic resonance spectroscopy
thf/THF	tetrahydrofuran
PEt_3	triethylphosphine
Ph	phenyl
py	pyridinyl
PyAp	deprotonated *N*-(2,6-di*iso*propylphenyl)-6-(pyrrolidin-1-yl)pyridin-2-amine
QTAIM	quantum theory of atoms in molecules
XRD	single crystal X-ray structure analysis

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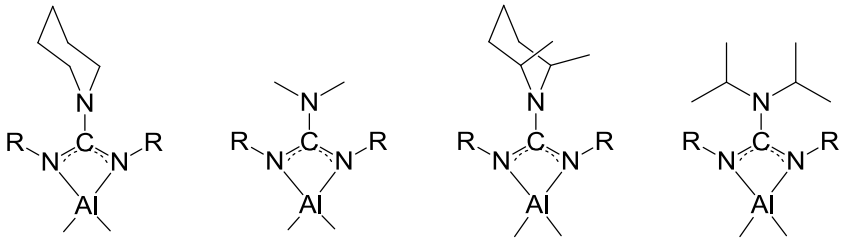
1 Summary/Zusammenfassung

1.1 Summary

The aim of this thesis was to synthesize (and characterize) group 3 and group 13 metal alkyl and hydride complexes. These complexes were supported by aminopyridinato, guanidinato and phenolato ligands. Guanidinato ligand stabilized aluminum alkyl complexes were synthesized through alkane elimination. Aminopyridinato and guanidinato ligand stabilized aluminum hydride complexes were synthesized using H_2 elimination. Mononuclear structures featuring tetrahedral coordination of the central aluminum atom were observed for the guanidinato ligand stabilized aluminum dialkyl complexes. The (Al)N-C-N(Al) bond angles in the corresponding complexes (Scheme 1.1) were determined using structural data. A decrease in the angle with increasing steric bulk of the ligands backbone was observed.



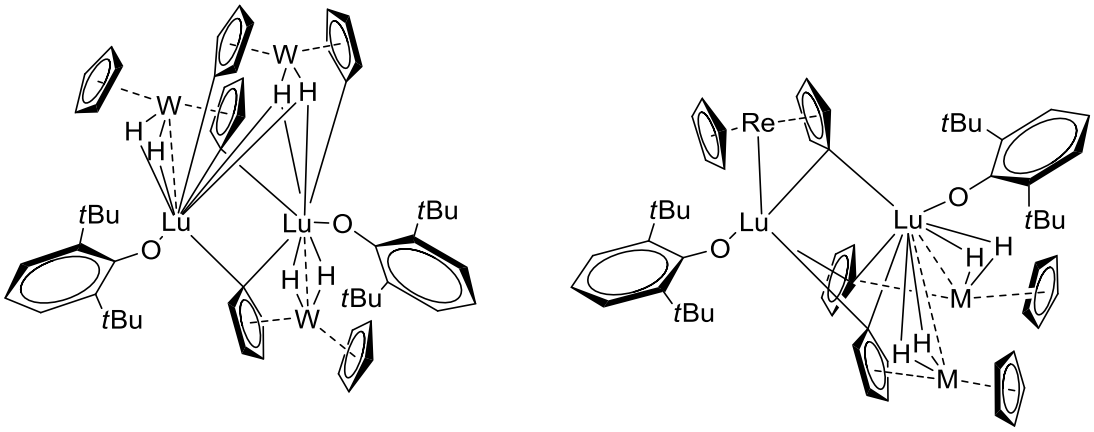
(Al)N-C-N(Al) angle (°)	109.8 (3)	109.47 (13)	107.68 (12)	107.39 (15)

Scheme 1.1. Experimentally observed (Al)N-C-N(Al) angles in guanidinato ligand stabilized aluminum dialkyl complexes (R = 2,6-di*iso*propylphenyl).

Studies regarding the dependency of the used aminopyridinato and guanidinato ligand on the structure and stability of aluminum hydride complexes were carried out. The prepared aminopyridinato ligand stabilized alane complex adopts a binuclear, double hydride bridged structure. The aluminum atoms are five-coordinated in this compound. This complex is thermally unstable. Intramolecular ligand redistribution reactions were observed even at room temperature resulting in a mononuclear aluminum monohydride complex stabilized by two aminopyridinato ligands. Again, the aluminum atom was five-coordinated in this compound. To obtain thermally stable complexes, guanidinato ligand stabilized aluminum hydride complexes were synthesized. Based on available literature, guanidinato ligands are not likely prone to follow ligand transfer reactions. If the guanidine PipGuH (*N,N*'-bis(2,6-di*iso*propylphenyl)piperidine-1-carboximidamide) is reacted with alane, an isostructural (to the

aminopyridinato ligand stabilized aluminum hydride complex) binuclear, double hydride bridged complex was observed. Moreover, the reaction of a bulky guanidine ligand with lithiumalanate was studied. Formation of a novel guanidinato ligand stabilized alanate complex (81 % yield) was observed. This is a rare example of a σ-alane lithium complex.

Guanidinato or phenolato ligand stabilized lanthanoid dialkyl complexes were synthesized starting from lanthanoid trialkyl complexes. These trialkyls were prepared by salt metathesis reaction of lithium alkyls with lanthanoid trichlorides. Hydrogenolysis with H_2 was used to convert the guanidinato ligand stabilized yttrium dialkyl complex into a trinuclear guanidinato ligand stabilized yttrium hexahydride cluster compound. This cluster compound was studied by single crystal X-ray structure analysis and NMR spectroscopy. Highly dynamic behavior of the hydrides and the guanidinato ligands was observed by variable temperature ^{1}H NMR spectroscopy. A heterobimetallic lutetium–tungsten polyhydride cluster compound (Scheme 1.2, left) was prepared by reaction of bis cyclopentadienyl tungsten dihydride with a phenolato ligand stabilized lutetium dialkyl complex. Cluster formation proceeded via C–H bond activation of the Cp ligands that stabilize the transition metal-containing educt followed by alkane elimination. Single crystal structure analysis revealed a cluster composed of three tungsten atoms and two lutetium atoms. Each of the two Lu atoms is double bridged by two μ_2-hydrides and two μ_3-hydrides to the W atoms. This finding was confirmed by ^{1}H NMR spectroscopy.



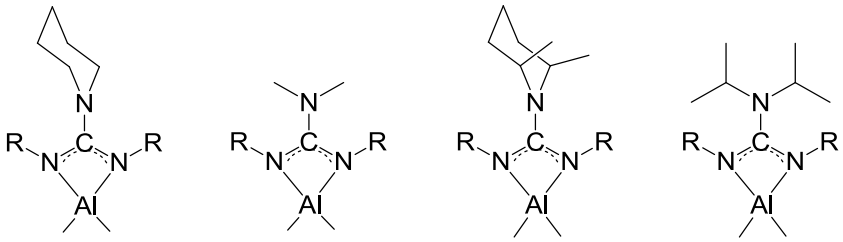
Scheme 1.2. Bi- and trimetallic polyhydride cluster compounds (M = Mo, W).

In addition, the first examples of ternary rare earth–transition metal polyhydride cluster compounds (Scheme 1.2, right) were synthesized starting from a phenolato ligand stabilized lutetium monoalkyl complex featuring a direct Lu–Re bond. Cluster formation proceeded by reaction with bis cyclopentadienyl tungsten dihydride or the analogue molybdenum compound. For both cluster compounds, the average yield was 50 %. Both of the ternary compounds were

characterized by single crystal structure analysis and NMR spectroscopy. These studies revealed isostructural clusters featuring two lutetium atoms, either two tungsten or two molybdenum atoms and a rhenium atom. The W and Mo atoms, respectively, are bridged by two μ_2-hydrides to the lutetium atoms. Quantum chemical calculations of the electronic structure, based on a simplified model (substituting H for the *tert*-butyl groups of the phenolato ligand) showed ionic W–H···Lu interactions and a covalent, polar Lu–Re bond.

1.2 Zusammenfassung

Das Ziel der vorliegenden Arbeit war die Synthese (und Charakterisierung) von Alkyl- und Hydridkomplexen der Metalle der 3. Gruppe und 13. Gruppe. Diese Komplexe sollten mit Aminopyridinato-, Guanidinato- und Phenolato-Liganden stabilisiert werden. Die Synthese der Guanidinato-Ligand-stabilisierten Aluminiumalkylkomplexe erfolgte mittels Alkaneliminierung. Die Aminopyridinato- bzw. Guanidinato-Ligand-stabilisierten Aluminiumhydridkomplexe wurden mittels H_2 Eliminierung dargestellt. Monomere Strukturen mit tetraedrischer Koordination um das zentrale Aluminiumatom wurden bei den Guanidinato-Ligand-stabilisierten Aluminiumdialkylen gefunden. Strukturelle Untersuchungen des (Al)N-C-N(Al)-Winkels (Abbildung 1.3) dieser Komplexe zeigten eine Abnahme des Winkels mit steigendem sterischen Anspruch im Rückgrat des Liganden.



(Al)N-C-N(Al)-Winkel in (°)	109.8 (3)	109.47 (13)	107.68 (12)	107.39 (15)

Abbildung 1.3: Experimentell bestimmte (Al)N-C-N(Al)-Winkel in den Guanidinato-Ligand-stabilisierten Aluminiumdialkylkomplexen (R = 2,6-Di*iso*propylphenyl).

Untersuchungen zur Abhängigkeit des verwendeten Aminopyridinato- bzw. Guanidinato-Liganden auf die resultierende Struktur und die Stabilität von Aluminiumhydridkomplexen wurden durchgeführt. Der hergestellte Aminopyridinato-Ligand-stabilisierte Aluminium-hydridkomplex weist eine dimere, doppelt hydridverbrückte Struktur auf. Die Aluminiumatome besitzen in dieser Verbindung die Koordinationszahl 5. Der erhaltene Komplex zeigt eine geringe thermische Stabilität. Es konnten bereits bei Raumtemperatur intramolekulare Ligandenübertragungsreaktionen beobachtet werden. Aus diesen Übertragungsreaktionen resultierte ein monomerer Aluminiummonohydridkomplex stabilisiert von zwei Aminopyridinato-Liganden. Das Aluminiumatom besitzt in dieser Verbindung ebenfalls die Koordinationszahl 5. Um thermisch stabile Komplexe zu erhalten, wurden Guanidinato-Ligand-stabilisierte Aluminiumhydridkomplexe hergestellt und untersucht. Es ist bekannt, dass Guanidinato-Liganden seltener zu Ligandenübertragungsreaktionen neigen. Bei der Reaktion von Aluminiumhydrid mit dem Guanidin PipGuH (*N,N*'-Bis(2,6-Di*iso*propylphenyl)piperidin-1-

Carboximidamid) wurde eine isostrukturelle Verbindung zu dem dimeren, Aminopyridinato-Ligand-stabilisierten Komplex erhalten. Des Weiteren wurde die Reaktion eines sterisch sehr anspruchsvollen Guanidinliganden gegenüber Lithiumalanat untersucht. Dabei wurde ein neuartiger, monomerer Guanidinato-Ligand-stabilisierter Aluminiumhydrid-Atkomplex in sehr guten Ausbeuten (81%) erhalten. Dies ist ein seltenes Beispiel eines σ-Alankomplexes von Lithium.

Die Synthese von Guanidinato- bzw. Phenolato-Ligand-stabilisierten Lanthanoid-dialkylkomplexen erfolgte ausgehend von Lanthanoidtrialkylen. Diese werden mittels Salzmetathesereaktion von Lithiumalkylen mit Lanthanoidtrichloriden gewonnen. Ausgehend von einem Guanidinato-Ligand-stabilisierten Yttriumdialkylkomplex konnte ein dreikerniger, Guanidinato-Ligand-stabilisierter Yttriumhexahydridkomplex mittels Hydrierung durch H_2 dargestellt werden. Die Clusterverbindung wurde mittels Röntgeneinkristallstrukturanalyse und NMR-Spektroskopie untersucht. Die ^{1}H-NMR-spektroskopischen Untersuchungen zeigten ein komplexes, dynamisches Verhalten der Hydrido- ebenso wie der Guanidinato-Liganden. Ausgehend von einem Phenolato-Ligand-stabilisierten Lutetiumdialkylkomplex wurde unter Verwendung von Bis-Cyclopentadienyl-Wolframdihydrid ein heterobimetallischer Lutetium–Wolfram-Polyhydridcluster hergestellt (Abbildung 1.4 links). Die Clusterbildung verläuft über mehrere C–H-Aktivierungen am Cyclopentadienyl-Liganden des Übergangsmetallfragments und anschließender Alkaneliminierung. Strukturelle Untersuchungen an dieser Verbindung offenbarten einen Cluster mit drei Wolframkernen und zwei Lutetiumkernen. Die beiden Lutetiumkerne sind jeweils doppelt μ_2-hydridverbrückt und doppelt μ_3-hydridverbrückt zu den Wolframkernen. Dies konnte durch ^{1}H-NMR-Spektroskopie belegt werden.

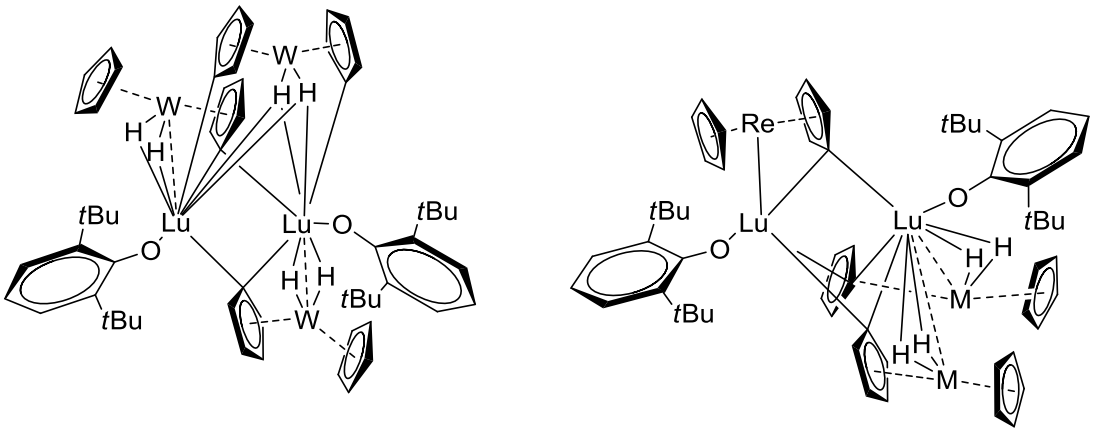


Abbildung 1.4: Bi- und trimetallische Polyhydridclusterverbindungen (M = Mo, W).

Darüber hinaus konnten die ersten Beispiele ternärer Polyhydridclusterverbindungen der Seltenen Erden dargestellt werden (Abbildung 1.4 rechts). Dies erfolgte ausgehend von einem

Phenolato-Ligand-stabilisierten Lutetiummonoalkylkomplex, welcher eine direkte Lu-Re-Bindung besitzt. Durch Reaktion mit Bis-Cyclopentadienyl-Wolfram- bzw. Molybdändihydrid konnten die Clusterverbindungen in guten Ausbeuten (ca. 50%) dargestellt werden. Die Verbindungen wurden mittels Röntgeneinkristallstrukturanalyse und NMR-Spektroskopie untersucht. Es zeigten sich isostrukturelle Cluster mit zwei Lutetium-, zwei Wolfram- oder Molybdänkernen und einem Rheniumkern. Die Wolfram- bzw. Molybdänkerne sind doppelt μ_2-hydridverbrückt zu den Lutetiumkernen. Quantenchemische Berechnungen der Bindungssituation an Hand einer minimal vereinfachten Modellstruktur (hierbei wurden die *tert*-Butylreste der Phenolato-Liganden durch H ersetzt) zeigten ionische Wolfram-Hydrid---Lutetium Wechselwirkungen und eine kovalente, polare Lu–Re-Bindung.

2 Introduction

Metal-carbon and metal-hydrogen bonds are at the very heart of coordination chemistry. Molecular metal hydrides, in general, are a fascinating class of compounds regarding their structure, reactivity and applications. They are key intermediates in a plethora of selective stoichiometric transformations and/or catalytic cycles. The first well-defined transition metal hydrides, $(CO)_4FeH_2$ and $(CO)_4CoH$, were prepared by Hieber and co-workers in 1931 and 1932, respectively.[1,2] These quite unstable compounds remained as laboratory curiosities for over 20 years. The next milestone dates back to the year 1955 with the discovery of $(C_5H_5)_2ReH$ by Birmingham and Wilkinson[3] and $(C_5H_5)(CO)_3MH$ (M = Cr, Mo, W) by Fischer and co-workers.[4] Two years later, Chatt, Duncanson, and Shaw prepared the exceptionally stable hydride compound *trans*-$(PEt_3)_2ClPtH$.[5] Since then, rapid development in this field took place and by the year 1965 over 200 derivatives were reported in some 300 publications.[6] In 2001 the Nobel Prize in chemistry was awarded jointly to Knowles, Nyori and Sharpless for asymmetric catalysis (Knowles and Nyori for contributions on asymmetric hydrogenation). This can be seen as one magic moment of metal hydride chemistry.

Research interest in the main group metal hydrides was documented alike.[7] The s-block metal hydrides are salt-like and the p-block metal hydrides form covalently bonded molecules comparable to the ones formed by the d- and f-block metals. Especially aluminum hydrides, first prepared by Stecher and Wiberg in 1942,[8] received much attention due to promising applications as reducing agents in organic synthesis[9] and for the reduction of metal complexes[10]. Furthermore, alanes are used in hydroamination reactions[11] and as precursors for metal organic chemical vapor deposition processes.[12] A more convenient preparation method was reported by Finholt, Bond, and Schlesinger in 1947.[13] Pioniering work on amine complexes of alane dates back to the early 1950s and the early 1960s.[14,15] Since then, much effort has been devoted to extend the field of alane chemistry. Transition metal σ-alane complexes[16] were prepared due to promising applications. Recent studies on alanes focus on applications as hydrogen storage materials.[17,18] Moreover, a guanidinato ligand stabilized adduct of dialane (Al_2H_4) was reported to feature a direct Al-Al bond.[19]

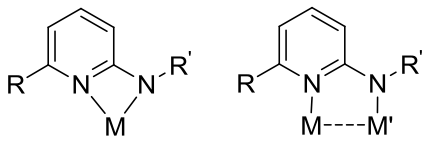
Another prominent and rich field of metal hydrides is found to be the hydrides of rare earth metals (group 3 metals and lanthanoid metals [Ce-Lu]). These compounds often aggregate and build up polyhydride clusters. Rare earth (poly)hydride compounds possess a fascinating variety of unique structural motifs and chemical properties. The early work on lanthanoid hydrides is reviewed by Bos and Gayer and covers the period from 1891 to 1966.[20]

Since then, it took over a decade until the first example of a molecular lanthanoid hydride was reported. Schumann and co-workers prepared $[(C_5H_5)_2LuH(thf)]$ (thf = tetrahydrofuran) by hydrogenolysis of the corresponding alkyl or aryl precursor in 1981.[21] From there on, research interest increased and an oddless number of cyclopentadienyl stabilized hydride and alkyl complexes of the rare earths became known.[22] Various applications and reactivities like hydrogenation reactions,[23] hydroboration reactions,[24] hydroamination reactions,[25] hydrosilylation reactions,[26] hydrophosphination reactions[27] and polymerization processes[28] of alkenes by cyclopentadienyl-type rare earth metal hydrides and alkyls are published. Hence, permanent interest in this type of compounds arose. Recently, a shift from cyclopentadienyl ligand sandwich- and half-sandwich (poly)hydride complexes towards alternatively supported hydride compounds has taken place.[29] Mainly, because of their promising new applications and reactivities. Nonetheless, rare earth metal hydride compounds supported by ligands other than Cp and its derivatives still lack in number.

The most used and important Cp alternatives are amido[30] (Scheme 1, right) and alkoxy ligands (Scheme 1, center). They have proven to be suitable for the stabilization of electron poor transition, main group and rare earth metal ions in different oxidation states.

Scheme 1. Commonly used ligand types for the stabilization of metal hydrides (R, R’ = aryl, alkyl or silyl, M = Main group, transition or rare earth metal).

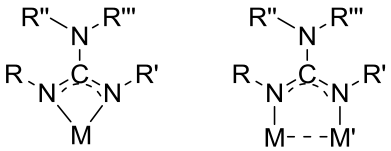
The aminopyridinato ligand, a subclass of the amido ligand family, derived from deprotonated 2-aminopyridines, has been prominently used in the renaissance of amido metal chemistry.[31] Two different binding modes are known (Scheme 2) and many substitution patterns to fine tune the steric bulk of the ligand are possible. Starting from 2,6-dibromopyridine, firstly a substituted phenyl group is introduced via Kumada coupling and secondly, a derivative of aniline is introduced via Buchwald-Hartwig aryl amination.



Scheme 2. Binding modes of aminopyridinato ligands (R, R' = aryl, alkyl or silyl, M = Main group, transition or rare earth metal, M' = transition metal).

$[Ru(PhNpy)_2)PPh_3)_2]$ was the first example of a strained η^2-coordinated aminopyridinato ligand stabilized complex, described by Cotton and co-workers in 1984.[32] In 1991 Gambarotta and co-workers reported on the first vanadium compound stabilized by an aminopyridinato ligand.[33] Kempe *et al.* prepared the first corresponding group 3 metal complex in 1997.[34]

Another subclass of the amido ligands are guanidinato ligands derived from deprotonated guanidines, which are comparable to the aminopyridinato ligands regarding their binding mode (Scheme 3). Their substitution pattern is more variable than for the aminopyridinato ligands, due to substitution on the nitrogen atoms. Recently, this ligand class was comprehensively reviewed by Jones.[35] Synthesis of guanidinato ligands is achieved via a direct approach starting from substituted carbodiimides, which are reacted, with lithiated secondary amine derivatives. The resulting lithium complexes of the ligands can be used in salt metathesis reactions towards metal halides or can be hydrolyzed to afford the protonated ligands. These protonated ligands can be used in alkane or amine elimination routes. Lappert and co-workers published the first transition metal guanidinato ligand stabilized complex in 1970.[36]



Scheme 3. Binding modes of guanidinato ligands (R, R',R'', R''' = aryl, alkyl or silyl, M = Main group, transition or rare earth metal, M' = transition metal).

Firstly, this work was focused on synthesis and characterization of guanidinato ligand stabilized aluminum dimethyl complexes. These complexes were examined regarding the substituents R'' and R'''. Dependency of the steric bulk towards the (M)N-C-N(M) angle was observed (Scheme 3, left, M = Al).

Secondly, synthesis and structure of Ap and Gu ligand stabilized Al-H complexes was discussed. The reaction of a sterically bulky guanidine with lithium alanate was examined. A rare example of a σ-alane lithium complex was observed.

Thirdly, a guanidinato ligand stabilized yttrium dialkyl complex was synthesized and characterized. Its ability towards hydrogenolysis using H_2 was investigated. The resulting trinuclear yttrium polyhydride cluster compound possesses highly dynamic behavior of the hydrides and the guanidinato ligands, as observed by variable temperature ^{1}H NMR spectroscopy.

Fourthly, the first examples of ternary rare earth-transition metal polyhydride cluster compounds were shown. Cluster formation proceeded through C–H bond activation of the Cp ligands that stabilize the transition metal-containing educt. Quantum chemical calculations of the electronic structure showed ionic W–H···Lu interactions and a covalent, polar Lu–Re bond.

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3 Overview of Thesis Results

This thesis comprises four publications, which are presented in chapters 4 to 7. The individual contributions to joint publications are pointed out in chapter 3.2. In the following, the central theme of the thesis is summarized.

3.1 Synopsis

The main task of this thesis was to increase the small number of structurally fully characterized group 3 and group 13 metal hydride compounds. Furthermore, group 3 and group 13 metal alkyl compounds were synthesized (and characterized). These alkyl compounds were synthesized as precursors and their ability to afford hydride compounds was studied. Supporting ligands for all complexes presented herein were restricted to aminopyridinato, guanidinato and phenolato ligands. These types of ligands are used to a very slight extent in group 3 and group 13 metal hydride chemistry. Chapter 4 deals with new aluminum alkyl compounds stabilized by guanidinato ligands. Guanidinato ligand stabilized aluminum dialkyls were synthesized and structurally characterized. Structural data of these compounds based on single crystal X-Ray structure analysis led to a concept of shortening metal-metal bonds. Due to this ligand based concept the best suited ligand yielding a stable Cr-Cr compound featuring the shortest metal-metal bond observed to date was found. In diguanidinato dichromium complexes the length of the quintuple bond can be influenced by the substituent at the central carbon atom of the used ligand. To find the guanidinato ligand forming the shortest Cr-Cr quintuple bonded complex, the dependency of the relevant N-C-N angle in the guanidinato ligand from the introduced substituent was investigated. Fine tuning of the ligands steric bulk was essential. Guanidinato ligand stabilized aluminum dialkyls were expected to be well suited for such a ligand fine-tuning. The tetrahedral coordination avoided inter-ligand repulsion and the smooth synthesis via alkane elimination from aluminum trialkyls allowed for an easy access. Four different guanidinato ligand stabilized aluminium dialkyls were synthesized. These compounds were isolated in good yields (> 80 %).

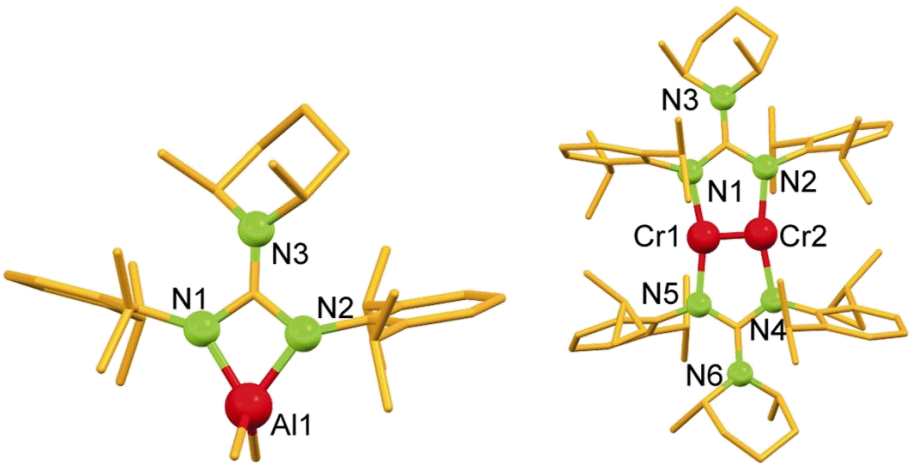


Figure 3.1. Crystal structure of [(MPipGu)AlMe$_2$] and [{(MPipGu)Cr}$_2$].

Structural data of the corresponding aluminum dialkyls showed promising (Al)N-C-N(Al) angles for the guanidinato ligands bearing a 2,6-dimethylpiperidine and a di*iso*propylamine backbone, respectively. The found (Al)N-C-N(Al) angles were 107.68(12)° (2,6-dimethylpiperidine) and 107.39(15)° (di*iso*propylamine). These two potential ligands were examined towards ultra short metal-metal distances.

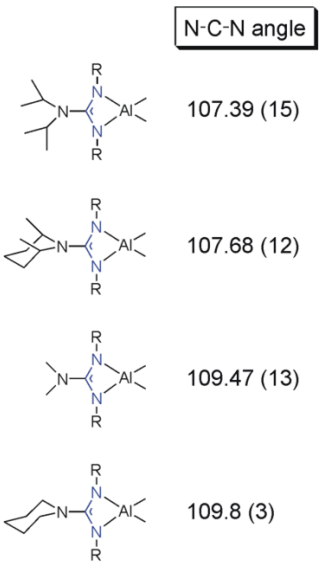


Figure 3.2.N-C-N angles for all structurally investigated Al complexes.

The guanidinato ligand carrying the 2,6-dimethylpiperidine backbone was found to be the optimal ligand. The reduction of its chromium(II) chloride ate-complex yielded a quintuply bonded bimetallic complex with a Cr-Cr-distance of 1.7056 (12) Å. Moreover, these guanidinato ligand stabilized aluminum dialkyls were thought of as precursors to aluminum hydride

compounds. Transformation of the alkyl compounds using H_2 and phenylsilane did not afford the corresponding hydride compounds. So, a direct approach to molecular alanes stabilized by N-ligands was carried out. Chapter 5 deals with the synthesis and structure of rare aminopyridinato and guanidinato ligand stabilized aluminum hydride compounds. Only a small number of structurally fully characterized amidinato, aminopyridinato and guanidinato ligand stabilized alanes are known until now. Starting from AlH_3, the direct approach to afford N-ligand stabilized aluminum hydride compounds was studied. The reaction of the aminopyridine *N*-(2,6-di*iso*propylphenyl)-6-(pyrrolidin-1-yl)pyridin-2-amine (PyApH) and the guanidine *N,N*'-bis(2,6-di*iso*propylphenyl)piperidine-1-carboximidamide (PipGuH) with freshly prepared AlH_3 was investigated. For both N-ligands the formation of a dimeric, double hydrogen bridged aluminum dihydride complex was observed. In these isostructural dimeric complexes, the aluminum centers are five-coordinated by two N atoms (from the N-ligands), two μ_2-bridging hydrides and a terminal hydride. The aminopyridinato ligand stabilized compound is unstable and intramolecular ligand redistribution reaction leading to monomeric $[(PyAp)_2AlH]$ was observed even at room temperature. The formation proceeded (most likely) via AlH_3 formation and its decomposition to Al and H_2. The guanidinato ligand stabilized complex was found to be more stable and no ligand transfer was observed up to 50°C. Furthermore, the reaction of (2R,6S,Z)-*N,N'*-bis(2,6-di*iso*propylphenyl)-2,6-dimethylpiperidine-1-carboximidamide (MPipGuH) with $LiAlH_4$ was examined. A rare example of a σ-alane lithium complex, namely $[(MPipGu)(H)_2Al(\mu\text{-}H)Li(thf)_3]$, was synthesized in 81 % yield.

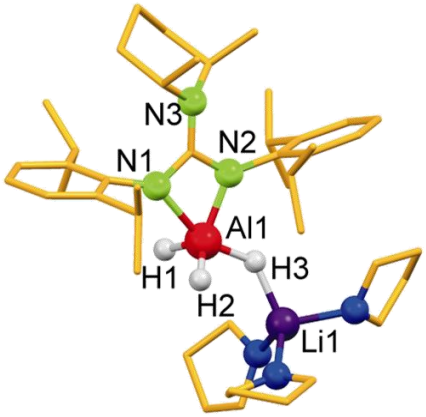


Figure 3.3. Crystal structure of the σ-alane lithium complex $[(MPipGu)(H)_2Al(\mu\text{-}H)Li(thf)_3]$.

In this compound, the aluminum center was five-coordinated. The guanidinato ligand was bound in a *N,N'*-dihapto-chelating mode. Two terminal hydrides and one bridging hydride to a THF stabilized lithium atom accomplished the coordination sphere around the aluminum atom. This complex could be a suitable precursor to synthesize other (example given) σ-alane

transition metal or σ-alane lanthanoid complexes. Based on the knowledge, that the guanidinato ligand stabilized aluminum dialykls were not able to undergo hydrogenolysis to afford the corresponding hydride compounds, examinations of group 3 metals were carried out. Chapter 6 deals with the synthesis and structure of a trinuclear yttrium polyhydride compound stabilized by a guanidinato ligand. The synthesis and structural determination of the first rare earth"$(LnH_2)_3$" polyhydride stabilized by a guanidinato ligand was achieved. An yttrium alkyl complex was thought of as a promising starting material and its behavior to hydrogenolysis using H_2 was examined. The reaction of equimolar amounts of yttrium trialkyl complex ($[YR_3(thf)_2]$) (R = $CH_2Si(CH_3)_3$, thf= tetrahydrofuran) with the guanidine *N,N'*-bis(2,6-di*iso*propylphenyl)piperidine-1-carboximidamide (PipGuH) gave the resulting guanidinato ligand stabilized yttrium dialkyl complex ([PipGu)YR_2(thf)]. This complex features a *N,N'*-dihapto-guanidinato ligand, two alkyl moieties and one THF molecule coordinated to the Y atom. In contrast to the aluminum dialkyl compounds, hydrogenolysis of this precursor with H_2 (2 bar) yielded clean formation of the corresponding guanidinato ligand stabilized trinuclear yttrium hexahydride cluster compound $[\{(PipGu)YH_2\}_3(thf)_2]$.

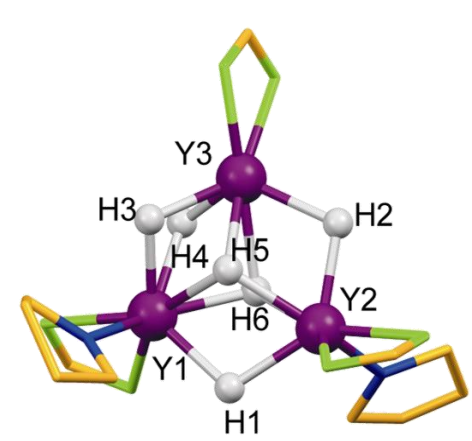


Figure 3.4. Crystal structure of the cluster core unit of $[\{(PipGu)YH_2\}_3(thf)_2]$ (guanidinato ligands only shown as NCN moieties for clarity).

The isolated yield was 96 %. Single crystal X-Ray structure analysis revealed a triangle defined by the three yttrium atoms. Each yttrium atom carried a guanidinato ligand in the same *N,N'*-dihapto-chelating mode like in the precursor dialkyl complex, as was revealed by XRD analysis. Moreover, coordinated THF molecules to two of the three yttrium atoms were found. Highly dynamic behaviour of the hydrido and the guanidinato ligands was observed by variable temperature ^{1}H NMR spectroscopy. Lanthanoid polyhydride cluster possess various, interesting structural motifs and, despite cyclopentadienyl ligand based compounds, are small in number. Moreover, a broad variety of applications are known. This type of compound was thought of as

educts for alkane elimination reactions using transition metal alkyl complexes. This could lead to heterobimetallic species. Vice versa, if transition metal hydride complexes are used in alkane elimination reactions with lutetium alkyl complexes, new heterobimetallic and ternary heteromultimetallic rare earth-transition metal polyhydride cluster compounds were observed. Chapter 7 deals with the synthesis and (electronic)structure of this type of compounds, especially on ternary rare earth-transition metal polyhydride compounds. Heteromultimetallic polyhydride complexes composed of rare earth metals and (late) transition metals are of great interest (example given) due to expected synergistic effects of the different metal centers. Only a rather small number of rare earth-transition metal polyhydride compounds are known. The reaction of $[Cp_2WH_2]$ (Cp = cyclopentadienyl) with lutetium dialkyl complex ($[Lu(OAr)R_2(thf)_2]$) (ArO = 2,6-di-*tert*-butyl-phenolate, R = $CH_2Si(CH_3)_3$, thf= tetrahydrofuran) gave the resulting heterobimetallic polyhydride cluster compound $[C_{58}H_{74}Lu_2O_2W_3]$. The compound showed poor solubility in aromatic solvents and was insoluble in aliphatic hydrocarbons. This cluster featured three tungsten centers and two lutetium centers, as was shown by X-ray crystal structure analysis. The reaction of group 6 metal dihydride complexes $[Cp_2MH_2]$ (Cp = cyclopentadienyl, M = Mo, W) with lutetium monoalkyl complex ($[Lu(OAr)(Cp_2Re)R(thf)]$) yielded the first example of ternary heteromultimetallic polyhydride clusters $[C_{58}H_{73}Lu_2O_2ReW_2]$ and $[C_{58}H_{73}Lu_2Mo_2O_2Re]$, respectively.

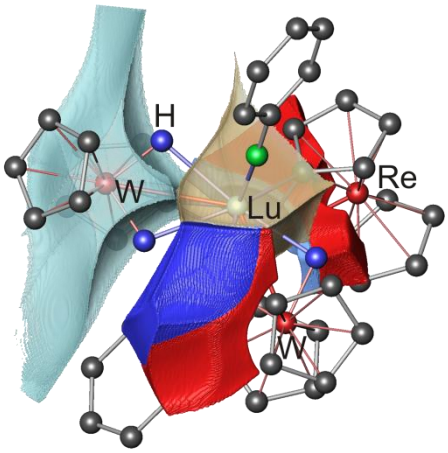


Figure 3.5.Optimized structure of the model compound $[C_{46}H_{49}Lu_2O_2ReW_2]$ with ELI-D/QTAIM basin intersections.

The isolated yield was 48 % for the tungsten compound and 52 % for the molybdenum compound. These cluster compounds were isostructural and featured two lutetium centers, with either two molybdenum or two tungsten centers and one rhenium center, as was shown by XRD analyses. The μ_2-bridging hydrides between the lutetium and the molybdenum or tungsten centers, respectively, were confirmed by ^1H NMR spectroscopy. Both compounds were well soluble in aromatic solvents and showed no solubility in aliphatic hydrocarbons. In these

compounds, three different metal centers are in close approximity and promising reactivities are thought of. Cluster formation proceeded via C–H bond activation of the Cp ligands that stabilize the transition metal-containing educt, followed by alkane elimination. Ionic hydrido supported W–H···Lu linkages and a covalent, polar Re–Lu bond were observed by quantum chemical calculations. Concerning the broader strategy of building higher aggregated ternary RE–TM polyhydride clusters an interesting and promising building block was found. Overall, this thesis introduces a lot of new group 3 and group 13 metal alkyl and hydride compounds in terms of synthetic and structural chemistry.

3.2 Individual Contribution to Joint Publications

All results presented in this thesis were obtained in collaboration with others and are published, accepted or to be submitted as indicated below. In the following, the contributions of all the co-authors to the different publications are specified. The asterisk denotes the corresponding author(s).

Chapter 4

This work is published in *Chem. Eur. J.* **2013,** *19*, 9825–9832 with the title

"The Ligand-Based Quintuple Bond-Shortening Concept and Some of its Limitations"

Awal Noor, Tobias Bauer, Tanya K. Todorova, Birgit Weber, Laura Gagliardi,* and Rhett Kempe*

Awal Noor synthesized the chromium compounds and carried out their corresponding characterization and has written the publication. I synthesized and characterized all of the aluminium compounds and the guanidine (PipGuH), carried out the corresponding NMR studies and did all of the XRD analyses of the aluminium and chromium compounds including structure solution and refinement. Moreover, I contributed to writing of the publication. Tanya K. Todorova and Laura Gagliardi did the theoretical calculations of the quintuple bonded Cr complexes and wrote the corresponding part of the publication. Birgit Weber did the Squid measurements and wrote the corresponding part of the publication. Rhett Kempe supervised this work and was involved in scientific discussions, comments and correction of the manuscript.

Chapter 5

This work is to be submitted with the title

"Synthesis and Structure of Aminopyridinato and Guanidinato Ligand stabilized Al-H Complexes"

Tobias Bauer, Winfried P. Kretschmer, Muhammad Hafeez, and Rhett Kempe*

I synthesized and characterized all of the compounds, carried out the NMR studies and the XRD analyses including structure solution and refinement except of the synthesis of the aminopyridine (PyApH), which was done by Muhammad Hafeez. The publication was written by me. Winfried P. Kretschmer was involved in scientific discussions. Rhett Kempe supervised this work and was involved in scientific discussions, comments and correction of the manuscript.

Chapter 6

This work is to be submitted with the title

"Synthesis and Structure of a Trinuclear Yttrium Polyhydride Cluster Stabilized by a Bulky Guanidinato Ligand"

Tobias Bauer, and Rhett Kempe*

I synthesized and characterized all of the compounds, carried out the NMR studies and the XRD analyses including structure solution and refinement. The publication was written by me. Rhett Kempe supervised this work and was involved in scientific discussions, comments and correction of the manuscript.

Chapter 7

This work is published in *Chem. Eur. J.* **2013**, *19*, 8732–8735 with the title

"Ternary Rare-Earth Transition Metal Polyhydride Cluster Compounds"

Tobias Bauer, Frank R. Wagner*, and Rhett Kempe*

I synthesized and characterized all of the compounds, carried out the NMR studies and the XRD analyses including structure solution and refinement. The publication was written by me except of the part on the quantum chemical calculations. Frank R. Wagner carried out the quantum chemical calculations presented in this work and has written this part of the publication. Rhett Kempe supervised this work and was involved in scientific discussions, comments and correction of the manuscript.

4 The Ligand-Based Quintuple Bond-Shortening Concept and Some of Its Limitations

Awal Noor,[a] Tobias Bauer,[a] Tanya K. Todorova,[b] Birgit Weber,[a] Laura Gagliardi, *[c]and Rhett Kempe*[a]

[a] Dr. A. Noor, T. Bauer, Prof. Dr. B. Weber, Prof. Dr. R. Kempe, Lehrstuhl Anorganische Chemie II, Universität Bayreuth, Universitätsstrasse 30, NW I, 95440 Bayreuth (Germany), Fax: (+49) 921552157, E-Mail: kempe@uni-bayreuth.de

[b] Dr. T. K. Todorova, Laboratory for Computational Molecular Design, Ecole Polytechnique Fédérale de Lausanne, Institut des Sciences et Ingénierie Chimiques CH-1015 Lausanne, (Switzerland).

[c] Prof. Dr. L. Gagliardi, Department of Chemistry, Supercomputing Institute, and Chemical Theory Center, University of Minnesota Minneapolis, Minnesota, 55455 (USA), E-mail: gagliard@umn.edu

Published in *Chem. Eur. J.* **2013,** *19*, 9825–9832.

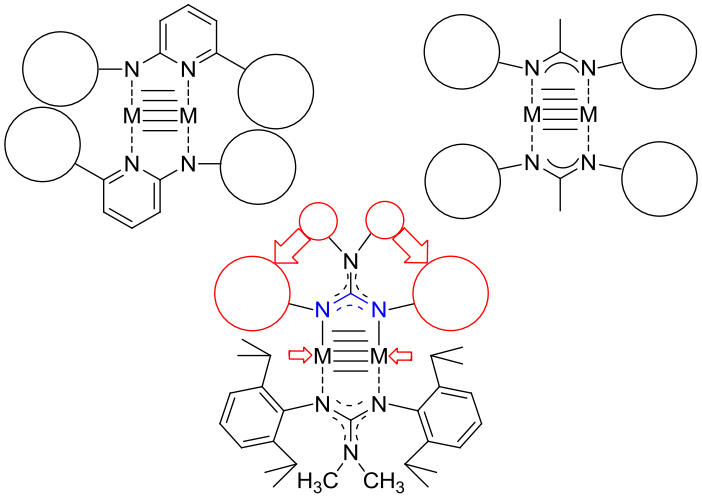
Keywords: chemical bonds • chromium • electronic structure • multiple bonds • N-ligands

Abstract: It is reported on the ligand based concept of shortening quintuple bonds and some of its limitations. In dichromium diguanidinato complexes the length of the quintuple bond can be influenced by the substituent at the central carbon atom of the used ligand. The guanidinato ligand carrying a 2,6-dimethylpiperidine backbone was found to be the optimal ligand. The reduction of its chromium(II) chloride ate-complex yielded a quintuply bonded bimetallic complex with a Cr-Cr-distance of 1.7056 (12) Å. Its metal-metal distance, the shortest observed in any stable compound yet, is of essentially the same length as that of the longest alkane C-C bond [1.704 (4) Å]. Both molecules, the alkane and the Cr complex, are of remarkable stability. Furthermore, an unsupported Cr(I) dimer with an EBO (= effective bond order) of 1.25 between the two metal atoms as indicated by CASSCF/CASPT2 calculations was isolated as a by-product. The formation of this by-product indicates that with a certain bulk of the guanidinato ligand other coordination isomers become relevant. Over-reduction takes place and a chromium arene sandwich complex structurally related to the

classic dibenzene chromium complex is observed if even bulkier substituents are introduced at the central carbon atom of the used guanidinato ligand.

4.1 Introduction

Bond orders are of fundamental importance in chemistry. The higher the bond order, the more electrons are “stored” in the linkage between the two atoms. These electrons can be used to form additional bonds and, as a consequence, to functionalize the bond or the compound. In this regard, compounds having exceptionally high bond orders are of special interest.[1] Furthermore, an increase in the bond order usually decreases the distance between the two linked atoms and transition metal and particularly chromium complexes having a high bond order are promising candidates to observe unusually short metal-metal distances.[1] The discovery of quadruple bonds about 50 years ago[2] led to decades of searching[3] for the shortest metal-metal bond (in a coordination compound). Koch & Cotton[4] re-synthesized[5] and Millar & Cotton[6] synthesized two very different di-chromium complexes having the same metal-metal distance of 1.83 Å. Interestingly, at the end of 2008 the Gambarotta group reported on a guanidinato chromium methyl complex with a quadruple bond of a length of 1.77 Å.[7] In 2005, the Power group found an elegant access[8] to coordination compounds having a Cr-Cr quintuple bond.[9] Surprisingly, the molecule they made had a metal-metal distance of 1.84 Å. The Theopold group could “solve” this contradiction, but more importantly showed that bulky monoanionic N-Ligands are well suited to stabilize quintuple bonds. They made a complex having a Cr-Cr distance of 1.80 Å.[10] Parallel, Power and co-workers showed that derivatives of their originally introduced compound could have a similar Cr-Cr distance.[11] Inspired by Theopolds work, the Tsai group and our group synthesized di-chromium amidinates[12] and aminopyridinates/guanidinates[13], respectively. Very short metal-metal distances, 1.73 Å (guanidinate), 1.74 Å (amidinate), and 1.75 Å (aminopyridinate) were observed.[14] A few conclusions can be drawn from these studies. Most importantly, the Cr-Cr distance seems to be strongly influenced by the stabilizing N-ligand (Scheme 1).In aminopyridinates (Scheme 1, left/top) the arrangement of the bulky aryl groups (large rings in Scheme 1) may cause inter-ligand repulsion limiting the “compression” of the two metals by the ligands. In amidinates (Scheme 1, right/top) and guanidinates (Scheme 1, bottom) the bulky aryl rings point away from each other lowering these inter-ligand repulsion. Furthermore, the steric pressure on top (marked red, Scheme 1) of the ligands may initiate a process that pushes the aryl rings down. As a consequence, the N-C-N angle (Scheme 1, marked blue) decreases and the N-centered lone pairs become aligned towards each other, which results in a shortening of the Cr–Cr distance (Scheme 1, bottom, red marked).

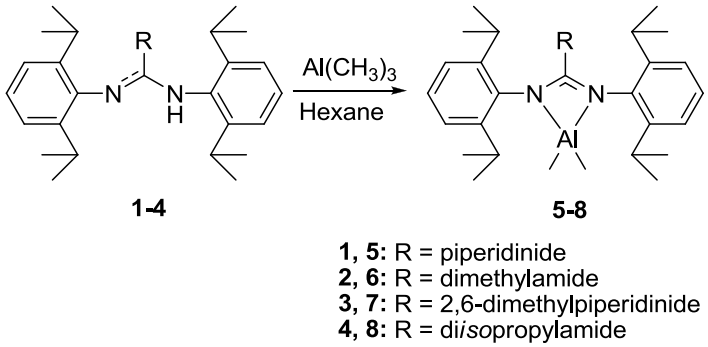


Scheme 1. The role of the stabilizing ligand on the metal-metal distance in complexes having a (formal) quintuple bond. The substituents on top (red) alter the N-C-N angle (blue) and compress the metal-metal multiple bond.

We report here the results of a systematic search for the shortest metal-metal (quintuple) bond. The finally obtained distance is 1.7056(12) Å. Furthermore, we point out at a few limitations of the above introduced ligand based metal-metal bond shortening concept, the main one being the formation of a different coordination isomer, an unsupported Cr(I) dimer with a significantly lower bond order. Quintuple bonding has gained a lot of attention meanwhile. The di-metallic (chromium or molybdenum) platform is well suited to activate small molecules.[15]

4.2 Results and Discussion

The hypothesis we developed from the state of the art in making ultra-short chromium-chromium quintuple bonds basically means the Cr-Cr distance is determined by the substituent R linked to the central carbon atom of the guanidinato (or amidinato) ligand (Scheme 2).



Scheme 2. Synthesis of the Al-complexes **5**-**8**.

In order to find the guanidinate ligand forming the shortest Cr-Cr quintuple bond the dependence of the relevant N-C-N angle in the guanidinate ligand from the introduced substituent R (Scheme 2) was investigated.

Aluminum dialkyls were expected to be well suited for such a study. The tetrahedral coordination avoids interference with the remaining ligands and the smooth synthesis via alkane elimination from commercially available trialkyls allows for an easy access. The aluminum guanidinates **5**-**8** (Scheme 2, Figure 1) were synthesized and characterized via X-ray crystal structure analysis. We observed that increasing the steric demand on the back bone from pipiridine to di*iso*propylamine decreases the NCN bond angle from 109.8(3) in **5** to 107.39(15) in **8** (Figure 1).[16] Thus, the ligands **3** and **4** should give Cr complexes with even shorter metal-metal bond distances than **2.** The Cr-Cr complex stabilized by **2** is featuring the shortest metal-metal bond [1.7293 (12) Å] observed in a stable molecule yet.[13b]

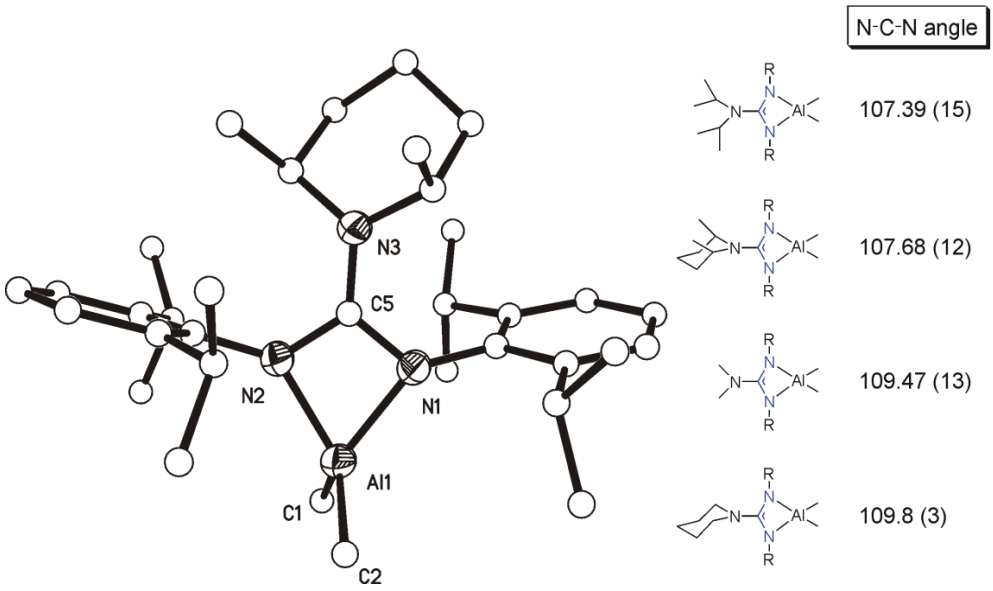
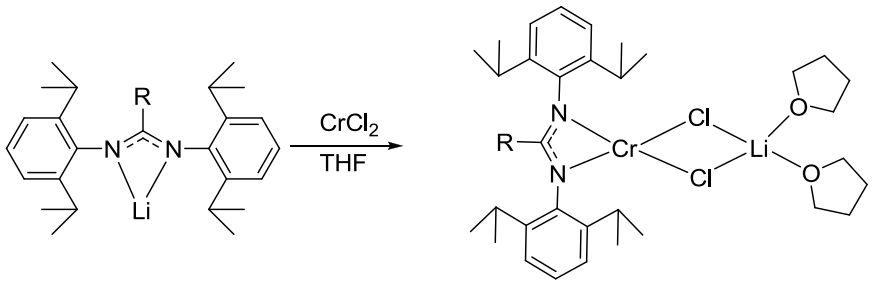


Figure 1.Molecular structure of **7** with the hydrogen atoms omitted for clarity and the crucial N-C-N angle for all structurally investigated Al complexes (R = 2,6-di*iso*propylphenyl).Selected bond lengths [Å] and angles [°]: Al1-N2 1.9245(13), Al1-N1 1.9318(13), Al1-C1 1.958(2), Al1-C2 1.9609(19); N2-C5-N1 107.68(12), N2-Al1-N1 69.09(5), N2-Al1-C1 113.78(7), N1-Al1-C1 120.33(8), N2-Al1-C2 118.70(7), N1-Al1-C2 113.44(7), C1-Al1-C2 114.32(9).

The reactions of the lithium guanidinates, Li[(2,6-dimethylpipiridine)C$(NAr)_2$] and Li[(di*iso*propylamine)C$(NAr)_2$][17] made from **3** and **4**, with $CrCl_2$ in THF afforded, after removal of the solvent and subsequent extraction with ether, the corresponding Cr(II) ate-complexes **9** and **10**, respectively as blue crystalline materials in good yields (Scheme 4).



9: R = 2,6-dimethylpipiridinide
10: R = di*iso*propylamide

Scheme 4. Synthesis of **9** and **10**.

The ^{1}H NMR spectra showed only broad signals due to the presence of paramagnetic Cr(II) ions. Both complexes were structurally investigated by X-ray crystal structure analysis. The observed structural motif has been recently reported for diketiminate ligands.[18] The molecular structure of **9** is shown in Figure 2. Its magnetic moments (μ_B) was determined to be 4.54. From the initially selected guanidines **3** and **4**, ligand precursor **4** carries the bulkiest substituent and for the corresponding Al complex **8** the smallest N-C-N angle was observed (Figure 1).

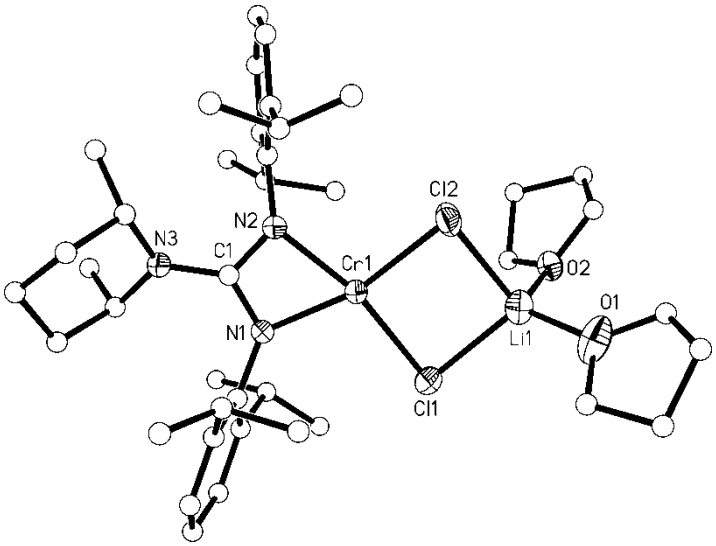
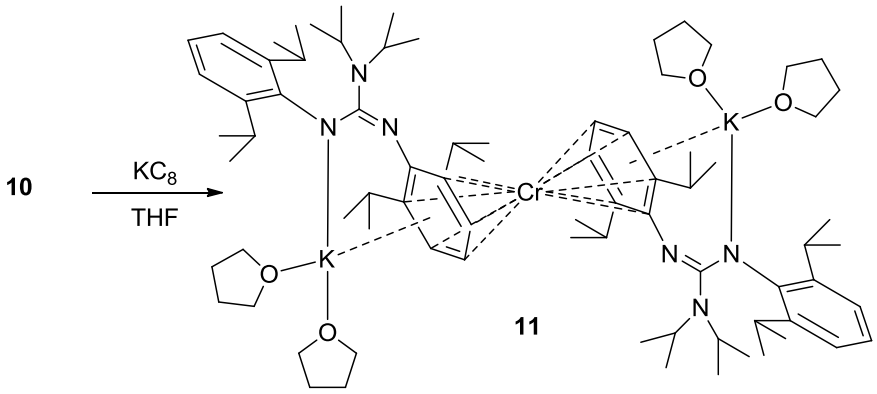


Figure 2. Molecular structure of 9 [ORTEP representation (on the 50 % probability level) for all non carbon atoms); Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-N1 1.348(2), C1-N2 1.352(3), C1-N3 1.375(3), Li1-O1 1.936(4), Li1-O2 1.941(4), Li1-Cl1 2.347(4), Li1-Cl2 2.361(4), Li1-Cr1 3.209(4), N1-Cr1 2.0527(16), N2-Cr1 2.0455(16), Cr1-Cl2 2.3492(6), Cr1-Cl1 2.3691(6); N1-C1-N2 109.73(16), N1-C1-N3 126.79(17), N2-C1-N3 123.48(17), N2-Cr1-N1 65.19(6), N2-Cr1-Cl2 99.46(5), N1-Cr1-Cl2 164.62(5), N1-Cr1-Cl1 101.51(5), Cl2-Cr1-Cl1 93.86(2).

Thus, we became interested to use **10**, which is stabilized by deprotonated **4**. The reduction of **10** with KC_8 and work up in hexane led to a monomeric Cr^0 complex (compound **11**, Scheme 5), in which the central Cr atom is sandwiched between two arene units of two guanidinate ligands (Figure 3).



Scheme 5. Synthesis of the Cr complex **11**.

Not only the η^6-coordination of the arene unit is limited to the bridging Cr, but the same arene unit also coordinates one K in the same fashion. Furthermore, the guanidinate ligands in **11** are acting as an amide coordinating the K atom through N1.

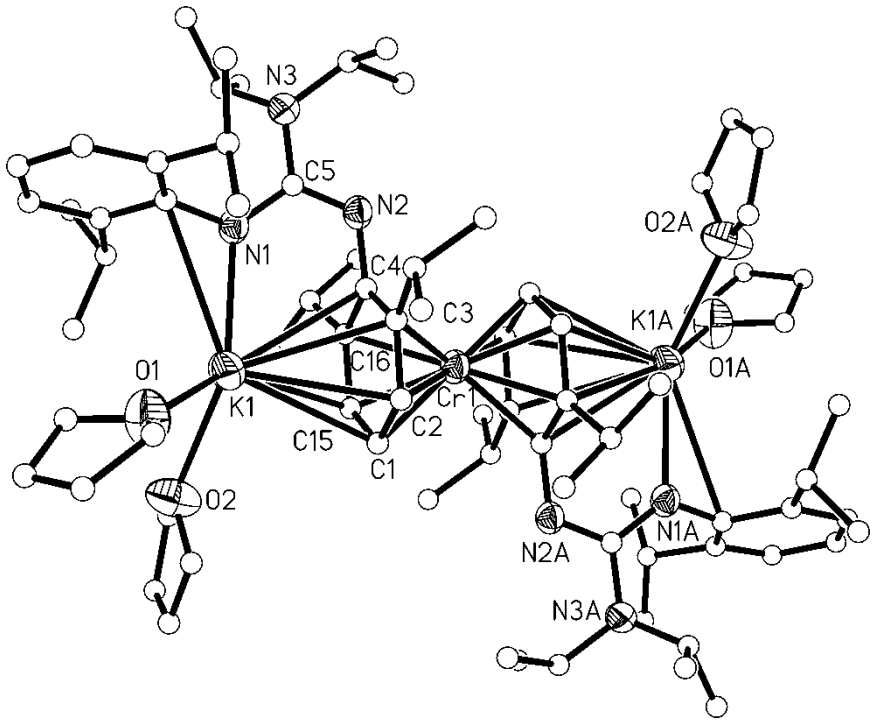
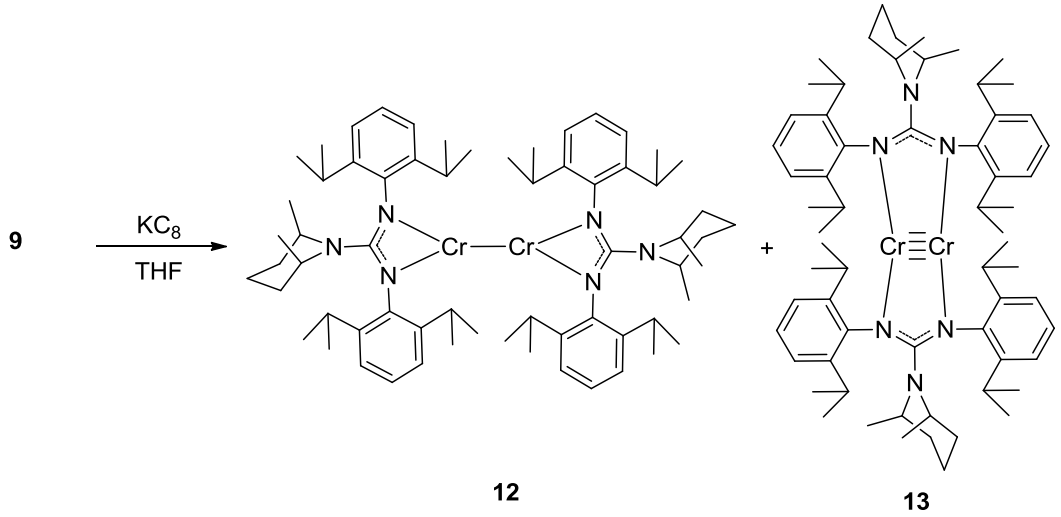


Figure 3. Molecular structure of **11**; Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]:C5-N2 1.310(5), C5-N1 1.359(5), C5-N3 1.424(6), N1-K1 2.688(4), Cr1–Ar centroid 1.667, K1–Ar centroid 2.798, O1-K1 2.682(4), O2-K1 2.748(4); N2-C5-N1 122.9(4), N2-C5-N3 117.3(4), N1-C5-N3 119.8(4), C5-N1-K1 129.6(3), O1-K1-N1 119.59(13), O1-K1-O2 82.70(13), N1-K1-O2 139.72(13).

The K atoms are further coordinated by two thf molecules. The central structural motif resembles the classic bis(benzene)chromium structure.[19] Since the reduction of **10** leads to an over-reduced product, we repeated the reaction more than five times also with varied amount of potassium graphite. The results were similar. We obtained **11** and leftover starting material (**10**) with lower amounts of the reducing agent. From these studies, we concluded that the steric bulk of the substituent in the backbone of **5** is already too large to stabilize a complex having a quintuple bond and continued with attempts based on **4** (or the dichloride **9**). Reduction of **9** with KC_8 in THF resulted in a sudden color change from royal blue to orange red (Scheme 6). After work up, **12** was isolated as purple needles at room temperature. The crystal structure of **12** reveals a compound where the two guanidinate ligands do not act as bridging ligands. They coordinate to each Cr atom in a chelating fashion giving rise to an unsupported Cr-Cr-bond. The Cr-Cr bond axis is collinear to the C_2 axis of NCN moiety of the guanidinate ligand. A Cr-Cr bond length of 2.652(2) Å is observed for **12**.



12 **13**

Scheme 6. Synthesis of **12** and **13**.

The molecular structure of **12** is shown in Figure 4. The conjugated NCN moiety shows very similar C-N distances [C1-N2 1.360(7), C1-N3 1.363(7), C1-N1 1.374(7) Å].

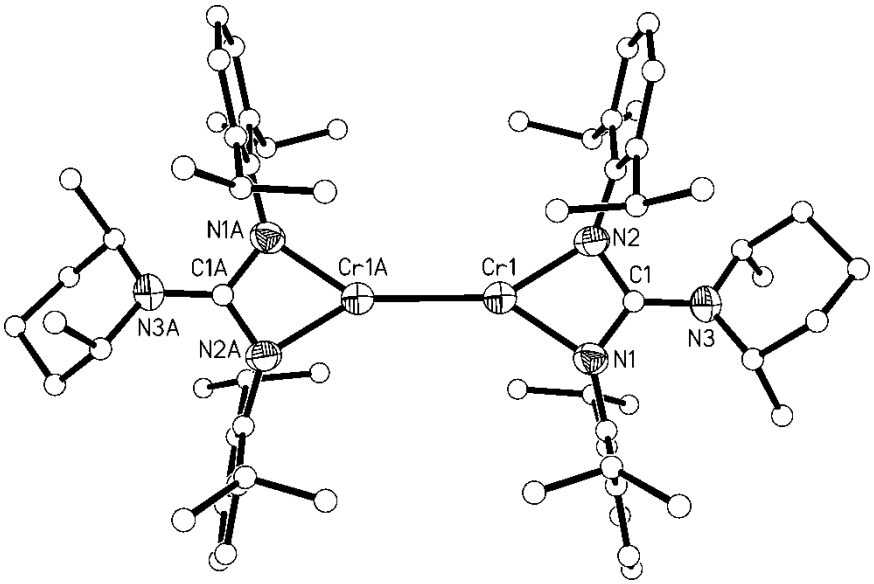


Figure 4. Molecular structure of **12**. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-N1 1.360(7), C1-N3 1.363(7), C1-N2 1.374(7), N1-Cr1 2.036(5), N2-Cr1 2.045(5), Cr1-Cr1 2.652(2); N1-C1-N3 125.5(6), N1-C1-N2 108.9(5), N3-C1-N2 125.5(6), N1-Cr1-N2 66.06(18), N1-Cr1-C1 32.84(18).

Unsupported chromium-chromium bonds are rare. Pioneering work in this regard was reported by the Gambarotta group.[20] They synthesized N-ligand stabilized Cr(II) with a rather weak bond between the two metal atoms. Dimers of Cr(I) such as those observed herein are difficult to obtain, because a variety of "side reactions" have to be avoided. Complexes of Cr(I) become mononuclear if the stabilizing ligand is too bulky.[11,21] Arene sandwich complexes can be formed if aromatic solvents are used.[22] The presence of dinitrogen can lead to N_2 complexes.[23] Furthermore, bridging of the aryl substituents of the N-ligand has to be avoided.[24] X-ray crystal structure analysis, magnetic data and electronic structural calculations (*vide infra*), IR data and reaction with CCl_4 (no formation of $CHCl_3$)[25] indicate that no bridging hydrides are present in **12**. Interestingly, the second and third crop of crystallization during the synthesis of **12** did not afford needles but orange red plates. The X-ray structural analysis revealed a bridged homobimetallic compound (**13**) with an exceptionally short metal-metal distance of 1.7056 (12) Å (Figure 5). A second crystal gave rise to a structure with a Cr-Cr distance of 1.7061(9) Å. It is the shortest Cr-Cr distance as well as the shortest metal-metal bond reported for a stable compound yet. A distance approaching 1.70 Å is interesting in a few regards. For instance, the chromium-chromium bond length of transient Cr_2 molecule which can be generated by laser-evaporation of the metal and via flash photolysis of $Cr(CO)_6$ is in the same distance range.[26,27] This compound has a formal sextuple bond. Furthermore, a similar distance as for the metal-metal bond in **13** was found recently for the longest alkane C-C bond[28] [1.704 (4) Å]. This essentially means a metal-metal bond and a C-C bond of an alkane can be of similar length. The Cr-N

bond lengths [1.992(4), 1.993(4), 2.008(4) and 2.011(4) Å] are comparable to the ones in the already known quintuply bonded chromium complexes but shorter than Cr-N bond distances [2.036(5) and 2.045(5) Å] observed for **12**.[7,9] The C-N bond distances [1.390(6) Á] for the non-coordinating nitrogen are slightly longer than the C-N bond distances of chromium coordinated nitrogen atoms [1.346(6) and 1.336(6) Å].

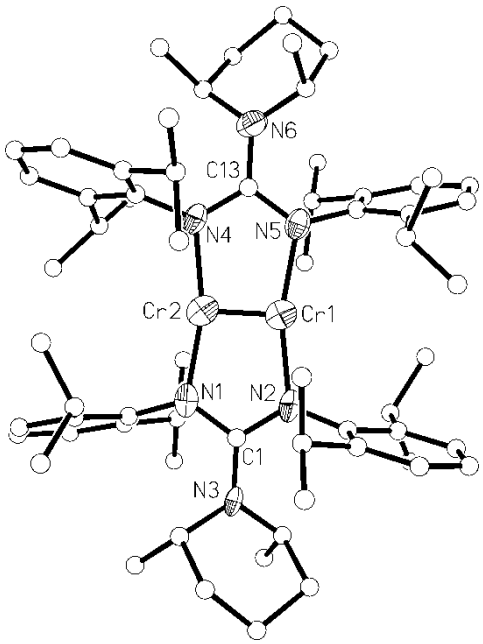


Figure 5. Molecular structure of **13**. Hydrogen atoms and one hexane molecule have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-N2 1.345(6), C1-N1 1.363(6), C1-N3 1.390(6), C13-N5 1.336(6), C13-N4 1.346(6), C13-N6 1.390(6), N1-Cr2 1.992(4), N2-Cr1 1.993(4), N4-Cr2 2.008(4), N5-Cr1 2.011(4), Cr1-Cr2 1.7056(12); N2-C1-N1 112.1(4), N2-C1-N3 124.1(4), N1-C1-N3 123.8(4), Cr2-Cr1-N2 98.27(12), N2-Cr1-N5 164.29(17), Cr1-Cr2-N1 97.26(12), N1-Cr2-N4 165.17(17).

Interestingly, parallel to our investigation the Jones group synthesized and characterized an iron(I) high-spin complex based on **3** with a very short Fe-Fe bond [2.1270(7) Å] that displays significant multiple-bond character.[29]

The room temperature magnetic moment of **12** is μ_B 4.66 which is higher than the theoretically expected value for two *S* = 2/2 chromium centers (theoretical value of μ_B = 4.00), but lower than the theoretical value for two *S* = 3/2 chromium centers (theoretical value of μ_B =5.48). This is in good agreement with a Cr-Cr bond with an effective bond order of 1.25 (*vide infra*), where two of the five electrons are involved in metal-metal bond formation. Upon cooling a continuous decrease of the magnetic moment down to μ_B 0.58 was observed. This behavior is best explained with antiferromagnetic interactions between the remaining unpaired electrons of the two chromium centers. The experimental data were fit assuming two antiferromagnetically coupled *S* = 3/2 centers with $H = -JS_1S_2$. The obtained coupling constant *J* = -62 (1) cm^{-1} (*g* = 2, TIP = 0.0013(1) $cm^3 \cdot mol^{-1}$) is indicative of strong

antiferromagnetic interactions between the two chromium centers. The room temperature magnetic moment of **13** is μ_B 2.27 which is indicative of an S = 0 ground state of the dinuclear chromium complex with a paramagnetic impurity (Chromium (I) with *S* = 5/2). This value does not change significantly upon cooling. The experimental data of **13** were fit assuming an *S* = 0 ground state and a temperature independent paramagnetism *TIP* due to Zeeman perturbation. The best fit for compound **13** was found with a paramagnetic impurity *PI* = 5.0 % per Cr (*S* = 5/2) and *TIP* = $787 \cdot 10^{-6}$ $cm^3 \cdot mol^{-1}$. Impurities in this %-range are not unusual for the very reactive quintuple bonds.[8,15a] In addition, herein, impurities of **12** may play a role.

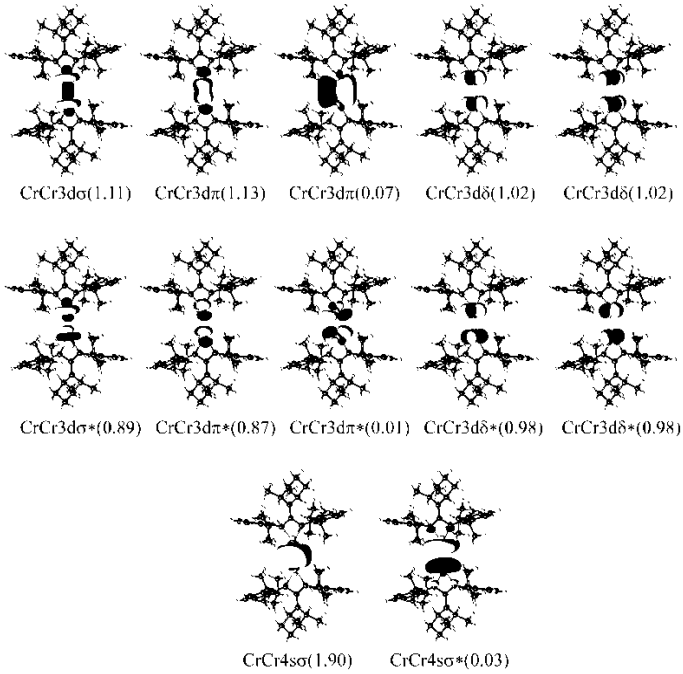


Figure 6.Active orbitals for structure **12** and their occupation numbers in the ground state.

Finally, multiconfigurational quantum chemical calculations using the CASSCF/CASPT2 method[30] were performed to examine the electronic structure of these two coexisting Cr_2-guanidinate compounds and in particular, the unique bonding of the unsupported Cr_2 unit in **12** and compared it to the bonding in **13**. Various dichromium systems, analogues to **13** are known to feature a quintuple metal-metal bond, despite the different ligands or oxidation state of the Cr atom. The metal-metal bonding is quantified in terms of effective bond order (EBO), defined as $(\eta_b - \eta_a)/(\eta_b + \eta_a)$, where η_b is the occupation number for the bonding natural orbital and η_a is the occupation number for the corresponding antibonding natural orbital. The ground state of **12** has a highly multiconfigurational singlet nature, which is practically degenerate (< 2 kcal/mol) with the triplet and quintet states. Inspection of the natural orbital occupation numbers (Figure 6) indicates that all the 3d orbitals, except one π/π^* pair, are singly occupied, which gives a minor contribution to the Cr-

Cr bond: the EBO value for the σ bond is 0.11, and the corresponding π and δ values are 0.16 and 0.04, respectively. One electron from each Cr atom is involved in Cr-N interaction with the ligands (those orbitals are not included in the complete active space). Interestingly, the strongest bond in the Cr_2 unit is the σ bond formed from the interaction of the 4s orbitals, with an EBO of 0.94. This results in a total bond order of 1.25 and an electronic configuration $(Cr\text{-}Cr)4s\sigma^2(Cr\text{-}Cr)3d\sigma^1(Cr\text{-}Cr)3d\sigma^{*1}(Cr\text{-}Cr)3d\pi^1(Cr\text{-}Cr)3d\pi^{*1}(Cr\text{-}Cr)3d\delta^2(Cr\text{-}Cr)3d\delta^{*2}$. Thus, the long 2.65 Å Cr-Cr bond in this unsupported Cr(I) dimer bears a single 4s–4s interaction with the 3d shells antiferromagnetically coupled into a net singlet state.

Table 1. Effective bond order for **12** and **13:**σ, π, δ contributions and total EBO values. Cr_2-guanidinate compound[13b] is given for comparison.

EBO	12	13	Cr2-guanidinate[31e]
σ	1.05	0.84	0.83
π	0.16	1.66	1.62
δ	0.04	1.43	1.35
Total bond order	1.25	3.93	3.80

In contrast to **12**, the short Cr-Cr bond in **13** is a formal quintuple bond with the Cr 3d orbitals forming the metal-metal multiple bond, whereas the pair of Cr 4s orbitals is directly involved in the Cr-N interaction with the ligands. The N atoms interact with the same weight with the Cr-Cr core as indicated by the shape of the Cr-N molecular orbitals (see Figure 7). The total EBO value of 3.93 (see Table 1) is slightly larger than the value of 3.80[31e] computed for the Cr_2-guanidinate system[13b] which holds the previous record for the shortest Cr-Cr bond. Inspection of Table 1 indicates that the shortening (ca. 0.02 Å) of the metal-metal bond is accompanied by a slight increase of the strength of one of the δ bonds. Analogously to other dichromium species,[31e,32] the closed-shell configuration $(Cr\text{-}Cr)3d\sigma^2(Cr\text{-}Cr)3d\pi^4(Cr\text{-}Cr)3d\delta^4(Cr\text{-}N)4s\sigma^2$ dominates the multideterminantal wave function with a total weight of 70 %.

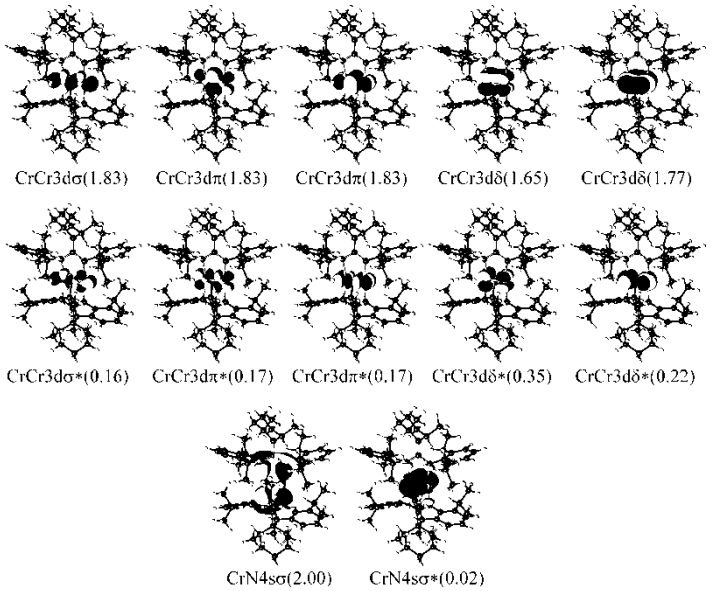


Figure 7.Active orbitals for structure **13** and their occupation numbers in the ground state.

The ^{1}H NMR of **13** shows well resolved single signal set indicative of a diamagnetic compound. Complex **12** is rather stable in solution and does not show any decomposition or conversion to **13** as monitored by NMR spectroscopy using a C_4D_8O solution.

4.3 Conclusions

In conclusion, we report on a rational approach to the complex having the shortest metal-metal bond. The key to isolate it, was a sterically tailor made guanidinate ligand. The metal-metal distance observed is of the same length as the longest C-C bond in stable alkanes. The ligand-based quintuple bond shortening concept has a few limitations. Most importantly, the formation of coordination isomers in which inter-ligand repulsion is minimized. It is assumable that additional shortening is difficult to accomplish since we reached the end of the stability gap.

4.4 Experimental Section

General: All manipulations were performed with rigorous exclusion of oxygen and moisture in Schlenk-type glassware on a dual manifold Schlenk line or in N_2 filled glove box (mBraun 120-G) with a high-capacity recirculator (<0.1ppm O_2). Solvents were dried by distillation from sodium wire / benzophenone. Commercial $CrCl_2$ (Alfa Aesor) was used as received. Compounds **2**, **3**, **4** and **8** were prepared according to published literature.[16,17a,33] Deuterated solvents were obtained from Cambridge Isotope Laboratories and were degassed, dried and distilled prior to use. NMR spectra were recorded on Varian 300 MHz and Varian 400 MHz at

ambient temperature. The chemical shifts are reported in ppm relative to the internal TMS. Elemental analyses (CHN) were determined using a Vario EL III instrument. X-ray crystal structure analyses were performed by using a STOE-IPDS II equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement was accomplished using SIR97,[34] SHELXL97[35] and WinGX.[36] CCDC-929720 (**5**), CCDC-929721 (**6**), CCDC-929719 (**7**), CCDC-814141 (**9**), CCDC-929718 (**10**), CCDC-929717 (**11**), CCDC-814142 (**12**) and CCDC-814143 (**13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Synthesis of compound 1:

To piperidine (0.37 mL, 5 mmol) in toluene (5 mL) was added *n*BuLi (2 mL of 2.5 M hexane solution, 5 mmol) at 0 °C and was stirred for 2.5 hours after the solution was warmed to room temperature. To this lithiated solution was then added bis-(2,6-di*iso*propyl-phenyl)-carbodiimide (1.81 g, 5 mmol) in toluene (15 mL) and the clear solution was stirred at room temperature overnight. All volatiles where removed under vacuum to give crude [Li(PipGu)] as an off white solid. Then Et_2O (20 mL), H_2O (5 mL) and EtOH (5 mL) was added and the two phases were separated. The aqueous phase was extracted with Et_2O (2 x 5 mL) and the combined organic phases where dried over Na_2SO_4 and filtered. Et_2O was removed under vacuum to give crude (PipGuH) as an off white solid. Yield: 2.187 g (98 %). Recrystallization from hexane at -40 °C gave colorless crystals of the product. Yield: 1.819 g (81 %). $C_{30}H_{45}N_3$ (447.70): Calcd. C 80.48, H 10.13, N 9.39; found. C 80.26, H 10.49, N 9.21; ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 0.94 (m, 4H, CH_2), 1.20 (m, 2H, CH_2), 1.25 – 1.40(m, 24H, CH(CH_3)$_2$, 3.05 (m, 4H, N(CH_2)$_2$), 3.31 (sept, 2H, CH(CH$_3$)$_2$), 3.45 (sept, 2H, CH(CH$_3$)$_2$), 5.24 (br s, 1H, NH) 7.07 – 7.34 (m, 6H, m-C$_5H_3$, p-C$_5H_3$). ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 13.30, 23.54, 24.45, 26.31, 28.29, 47.54, 124.01, 125.67, 126.54, 137.96, 139.27, 144.67, 163.46.

Synthesis of compound 5:

To a solution of (PipGuH) (0.90 g, 2 mmol) in hexane (5 mL) was added trimethylaluminum (0.84 mL of 2.5 M hexane solution, 2.1 mmol) at 0 °C. The resulting pale yellow solution was warmed to room temperature slowly and stirred overnight. Then, the clear, pale yellow solution was concentrated under vacuum to afford colorless crystals at room temperature. Yield: 0.847 g (84 %). $C_{32}H_{50}AlN_3$ (503.74): Calcd. C 76.30, H 10.00, N 8.34; found. C 76.11, H 10.24, N 7.61 ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = - 0.12 (s, 6H, CH_3), 0.91 (m, 4H, CH_2), 1.27 (m, 2H, CH_2), 1.35 (d, 24H, CH(CH_3)$_2$, 2.77 (m, 4H, N(CH_2)$_2$), 3.73 (sept, 4H,

C*H*$(CH_3)_2$), 7.07 – 7.34 (m, 6H, m-C_5H_3, p-C_5H_3). ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = -8.42 (br), 23.55, 24.45, 26.32, 28.29, 47.55, 124.01, 125.68, 126.54, 137.96, 139.26, 144.66, 163.46.

Synthesis of compound 6:

(Me_2NGuH) (0.82 g, 2 mmol) was solved in hexane (5 mL) and trimethylaluminum (0.84 mL of 2.5 M hexane solution, 2.1 mmol) was added at 0 °C. The reaction mixture was then slowly allowed to warm to room temperature and was stirred overnight. The resulting pale yellow solution was concentrated under reduced pressure to afford colorless crystals of the product at room temperature. Yield: 0.788 g (85 %). $C_{29}H_{46}AlN_3$ (463.68): Calcd. C 75.12, H 10.00, N 9.06; found. C 75.13, H 10.02, N 8.90; ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = - 0.15 (br s, 6H, C*H*$_3$), 1.25 (d, 12H, J_{HH} = 6.91 Hz; CH(C*H*$_3$)$_2$), 1.35 (d, 12H, J_{HH} = 6.75 Hz; CH(C*H*$_3$)$_2$), 2.07 (s, 6H, N(C*H*$_3$)$_2$, 3.67 (sept, 4H,J_{HH} = 6.84 Hz, C*H*$(CH_3)_2$, 7.08 – 7.22 (m, 6H, m-C_6H_3, p-C_6H_3) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = -9.6 (br), 23.25, 25.90, 28.29, 38.66, 123.93, 125.47, 139.16, 144.31, 163.82.

Synthesis of compound 7:

Trimethylaluminum (0.44 mL of 2.5 M hexane solution, 1.1 mmol) was added to a hexane (3 mL) solution of (MPipGuH) (0.476 g, 1 mmol) at 0 °C and the resulting reaction mixture was afterwards slowly warmed to room temperature and stirred overnight. Then the solvent volume was reduced under vacuum and colorless crystals formed at room temperature. Yield: 0.443 g (83 %). $C_{34}H_{54}AlN_3$ (531.79). Calcd. C 76.79, H 10.23, N 7.90; found. C 76.30, H 10.16, N 7.84; ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = - 0.08 (br s, 6H, C*H*$_3$), 0.77 (d, 6H, J_{HH} = 7.11 Hz, N[CH(C*H*$_3$)]$_2$), 0.84-1.06 (br m, 6H, piperidine-C*H*$_2$C*H*$_2$C*H*$_2$), 1.35 (d, 12H, J_{HH} = 6.68 Hz, CH(C*H*$_3$)$_2$), 1.39 (d, 12H, J_{HH} = 6.92 Hz, CH(C*H*$_3$)$_2$), 3.80 (sept, 4H, J_{HH} = 6.78 Hz, C*H*$(CH_3)_2$, 3.92 (sept, 2H, J_{HH} = 6.05 Hz, N[C*H*$(CH_3)]_2$), 7.14 - 7.21 (br m, 6H, m-C_6H_3, *p*-C_6H_3) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = -7.13 (br), 13.35, 21.24, 23.46, 27.21, 28.44, 29.51, 48.40, 124.09 125.87, 139.35, 145.48, 164.10.

Synthesis of compound 9:

*n*BuLi (6.25 mL of 1.6 M hexane solution, 10 mmol) was added to 2,6-dimethylpiperidine (1.13 g, 10 mmol) in THF (20 mL) at 0 °C and the solution was then warmed to room temperature and stirred for 4 hours. The lithiated solution was then added to bis-(2,6-di*iso*propyl-phenyl)-carbodiimide (3.63 g, 10 mmol) in THF (10 mL) and stirred overnight. The clear solution was then added to $CrCl_2$ (1.23 g, 10 mmol) in THF (5 mL) at 0 °C and then stirred at 50 °C overnight. THF was removed under vacuum and product was extract with

ether (2 x 30 mL). The blue solution was concentrated under vacuum to afford blue crystals of the product at low temperature. Yield: 3.950 g (53 %). $C_{40}H_{64}Cl_2CrLiN_3O_2$ (748.80): Calcd. C 64.16, H 8.61, N 5.61; found. C 64.01, H 8.16, N 5.58. μeff(294.3 K) = 3.91 μB. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 0.61 (br s), 1.10 (s), 1.46 (br s), 3.25 (s), 3.58 (v br s), 4.98 (v br s), 6.32 (br s), 13.31 (br s) ppm.

Synthesis of compound 10:

THF (20 mL) was added to bis-(2,6-di*iso*propyl-phenyl)-carbodiimide (1.089 g, 3 mmol) and LiN[CH(CH_3)$_2$] (0.321 g, 3 mmol) and the solution was then stirred for 4 hours. The clear solution was then added to $CrCl_2$ (0.369 g, 3 mmol) in THF (5 mL) at 0 °C and the resulting blue solution was then stirred at 50 °C overnight. THF was removed under vacuum and product was extract with ether (2 x 30 mL). The blue solution was concentrated under vacuum to afford blue crystals of the product at room temperature. The crystals were washed with hexane (2 x 15 mL). Yield: 1.13 g (51 %). $C_{39}H_{64}Cl_2CrLiN_3O_2$ (736.79): Calcd. C 63.58, H 8.76, N 5.70; found. C 63.71, H 8.61, N 6.11. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 0.88 (br s), 1.24 (s), 1.41 (br s), 3. 47 (s), 3.57 (v br s), 4.98 (v br s), 6.38 (v br s), 13.11 (br s) ppm.

Synthesis of compound 11:

Complex **10** (1.650 g, 2.24 mmol) in THF (15 mL) was added to one and a half equivalent of freshly prepared KC_8 in THF (20 mL) at -30 °C. The resulting brown red suspension was then stirred overnight at room temperature. THF was removed under vacuum and product was extract with hexane (25 mL). The dark red filtrate was allowed to afford needles of **11** at room temperature. Yield: 0.254 g (19 %). $C_{78}H_{128}CrK_2N_6O_4$ (1344.08): Calcd. C 69.70, H 9.60, N 6.25; found. C 69.00, H 9.72, N 5.80. ^{1}H NMR (400 MHz, C_6D_8O, 298 K): δ = 0.69-1.40 (m, 60 H, CH(CH_3)$_2$), 1.50 (d, *J* = 6.8 Hz, 3H, CH(CH_3)$_2$), 1.60 (d, *J* = 6.8 Hz, 3H, CH(CH_3)$_2$), 1.69 (br s,16H, OCH_2CH_2'), 1.84 (d, *J* = 6.8 Hz, 6H, CH(CH_3)$_2$), 3.16 (sep, 1H, *J* = 6.8 Hz, C*H*(CH_3)$_2$), 3.30-3.49 (m, 8H, *CH*(CH_3)$_2$), 3.54 (br s,16H, OCH_2CH_2), 3.64-3.81 (m, 3H, *CH*(CH_3)$_2$), 4.21 (t, 1H, C_6H_5), 4.30 (t, 1H, C_6H_5), 4.36 (d, 1H, C_6H_5), 4.61 (d, 1H, C_6H_5), 4.70 (d, 1H, C_6H_5), 4.76 (d, 1H, C_6H_5), 5.22 (d, 1H, C_6H_5), 6.43 (br t, 1H, C_6H_5), 6.72 (m, 2H, C_6H_5), 6.87 (d, 1H, C_6H_5), 7.06 (d, 1H, C_6H_5), 7.21 (br t, 1H, C_6H_5) ppm.

Synthesis of compounds 12 and 13:

Complex **9** (2.070 g, 2.76 mmol) in THF (15 mL) was added to one and a half equivalent of freshly prepared KC_8 in THF (20 mL) at -30 °C. The resulting brown red suspension was then stirred overnight at room temperature. THF was removed under vacuum and product was extract with hexane (30 mL). The dark red filtrate was allowed to afford needles of **12** at room

temperature. Yield: 0.045 g (4.27 %). $C_{64}H_{96}Cr_2N_6$ (1053.48): Calcd. C 72.97, H 9.19, N 7.98; found. C 72.19, H 9.33, N 7.49. ^{1}H NMR (400 MHz, C_4D_8O, 298 K): δ = 0.65-1.44 (br m, 36H, NCHCH_3,CH(CH_3)$_2$), 2.04 (br s, 24H, CH(CH_3)$_2$), 3.39-3.97 (m, 24H, CH,CH_2,CH(CH_3)$_2$), 6.98-7.00 (br m, 4H, H^{meta}), 7.82 (br s, 2H, H^{para}) ppm.

The solution was then filtered and allowed to give red plates of **13** at room temperature. Yield: 0.321 g (3 crops, 28.17 %). $C_{64}H_{96}Cr_2N_6.C_6H_{12}$ (1139.65): Calcd. C 73.77, H 9.73, N 7.37; found. C 73.60, H 9.70, N 7.42. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = -1.05 (d, 12H, *J* = 6.2 Hz, CH(CH_3)$_2$), 0.67 (d, 6H, *J* = 6.7 Hz, NCHCH_3), 1.16 (d, 12H, *J* = 6.8 Hz, CH(CH_3)$_2$), 1.25-1.42 (m, 12H, CH_2), 1.52 (d, 6H, *J* = 6.7 Hz, NCHCH_3), 1.74 (d, 12H, *J* = 6.8 Hz, CH(CH_3)$_2$), 2.28 (br d, 12H, CH(CH_3)$_2$), 3.28 (br m, 4H, C*H*(CH$_3$)$_2$), 4.64 (m, 2H, NC*H*), 4.77 (m, 2H, NC*H*), 5.00 (sep, 4H, *J* = 6.2 Hz, C*H*(CH$_3$)$_2$), 6.46 (d, 4H, *J* = 7.5 Hz, H^{meta}), 6.76 (t, 4H, *J* = 7.5 Hz, H^{para}), 7.03 (d, 4H, *J* = 7.5 Hz, H^{meta}) ppm. ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ = 20.5 (NCH*C*H$_3$), 23.0 (NCH*C*H$_3$), 23.0 (CH(*C*H$_3$)$_2$), 23.6 (CH(*C*H$_3$)$_2$), 28.6 (*C*H(CH$_3$)$_2$), 28.9 (*C*H(CH$_3$)$_2$), 29.1 (CH(*C*H$_3$)$_2$), 31.1 (*C*H2), 48.5 (N*C*H), 51.2 (N*C*H), 123.5 (C^{meta}), 123.7 (C^{para}), 124.0 (C^{meta}), 142.4 (C^{ipso}), 143.0 (C^{ipso}), 144.0 (C^{ortho}), 166.5 (N*C*N) ppm.

4.5 Acknowledgments

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4.7 Supporting Information

X-ray crystallographic data including tables, details of the magnetic and computational study

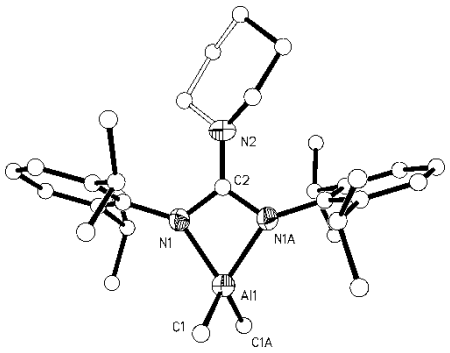

Figure S1. Molecular structure of **5** [ORTEP representation (on the 50 % probability level) for all non carbon atoms]; Hydrogen atoms have been omitted for clarity.

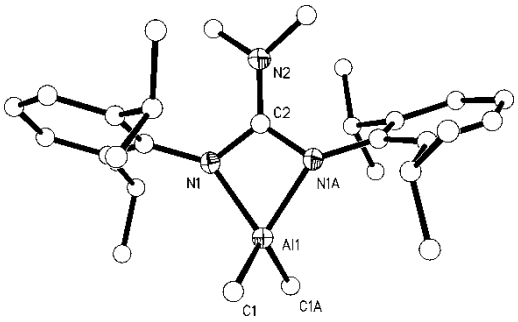

Figure S2. Molecular structure of **6** [ORTEP representation (on the 50 % probability level) for all non carbon atoms]; Hydrogen atoms have been omitted for clarity.

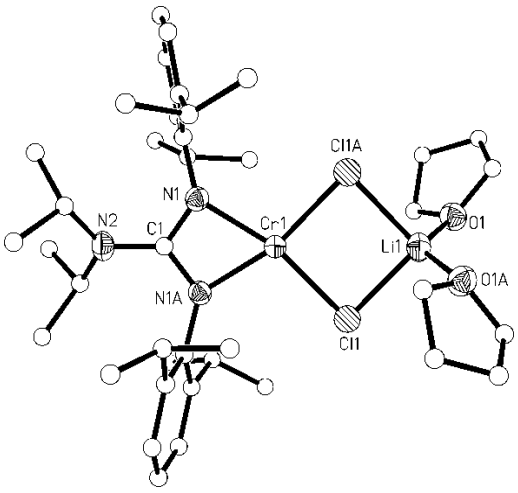

Figure S3. Molecular structure of **10** [ORTEP representation (on the 50 % probability level) for all non carbon atoms]; Hydrogen atoms have been omitted for clarity.

Table S1. Crystal data for Al compounds **5**, **6** and **7**.

compound	5	6	7
Empirical formula	$C_{32}H_{50}AlN_3$	$C_{29}H_{46}AlN_3$	$C_{34}H_{54}AlN_3$
Formula weight	503.73	463.67	531.78
crystal system	Hexagonal	Hexagonal	Monoclinic
space group	P3(2)21	P3(2)21	P2(1)/c
a [Å]	14.9090(7)	14.4200(6)	9.4030(5)
b [Å]	14.9090(7)	14.4200(6)	31.9350(17)
c [Å]	12.2510(6)	12.2130(5)	11.2800(6)
α [deg]			
β [deg]			106.059(4)
γ [deg]			
V, [$Å^3$]	2358.30(19)	2199.29(16)	3255.0(3)
crystal size, [mm^3]	0.41 x 0.36 x 0.35	0.34 × 0.33 × 0.29	0.67 x 0.55 x 0.48
ρ_{calcd}, [g cm^{-3}]	1.064	1.050	1.085
μ, [mm^{-1}] (Mo Kα)	0.087	0.089	0.088
T, [K]	133(2)	133(2)	133(2)
θ range, [deg]	1.58- 25.69	1.63- 25.60	1.28- 25.80
no. of reflections unique	2991	2769	6171
no. of reflections obs. [I > 2σ (I)]	2394	2580	5293
no. of parameters	187	157	343
wR^2 (all data)	0.1083	0.0785	0.1226
R value [I>2σ (I)]	0.0463	0.0352	0.0477

Table S2. Crystal data for Cr compounds **9**, **10**, **11**, **12** and **13**.

compound	9	10	11	12	13
Empirical formula	$C_{40}H_{64}Cl_2CrLiN_3O_2$	$C_{39}H_{64}Cl_2CrLiN_3O_2$	$C_{78}H_{128}CrK_2N_6O_4$	$C_{64}H_{96}Cr_2N_6$	$C_{70}H_{108}Cr_2N_6$
Formula weight	748.78	736.77	1344.06	526.73	1137.62
crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
space group	P-1	C2/c	P2(1)/n	P-1	P-1
a [Å]	11.2860(6)	16.0290(5)	10.6720(6)	10.8060(8)	12.6160(5)
b [Å]	13.7030(6)	16.4480(5)	18.8650(10)	10.9290(9)	15.1330(6)
c [Å]	14.689(8)	16.8070(7)	20.0340(10)	15.8220(12)	19.4170(7)
α [deg]	102.318(4)			90.514(6)	112.679(3)
β [deg]	94.489(4)	108.140(3)	104.381(4)	70.900(6)	95.143(3)
γ [deg]	107.100(4)			69.395(6)	98.334(3)
V, [$Å^3$]	2096.95(18)	4210.8(3)	3907.0(4)	1601.6(2)	3341.0(2)
crystal size, [mm^3]	0.36 x 0.32 x 0.24	0.23 x 0.21 x 0.18	0.42 x 0.27 x 0.07	0.31 x 0.29 x 0.15	0.21 × 0.20 × 0.12
ρ_{calcd}, [g cm^{-3}]	1.186	1.162	1.142	1.092	1.131
μ, [mm^{-1}] (Mo Kα)	0.435	0.432	0.302	0.379	0.368
T, [K]	133(2)	133(2)	133(2)	193(2)	133(2)
θ range, [deg]	1.44-25.67	1.82-25.67	1.51-25.67	2.49-25.66	1.15-25.69
no. of reflections unique	7899	3961	7380	6018	12613
no. of reflections obs. [I > 2σ (I)]	6333	2919	3630	1959	4306
no. of parameters	442	219	424	335	694
wR^2 (all data)	0.1120	0.1025	0.1781	0.1685	0.1419
R value [I>2σ (I)]	0.0418	0.0463	0.0794	0.0718	0.0611

Susceptibility measurements: Magnetic susceptibility measurements were carried out with a Quantum Design MPMS-XL SQUID magnetometer in the range from 2 to 300 K at 2 T (**12**) and 0.5 T (**13**). The powdered sample **12** was placed in a gelatin capsule, fixed in a non-magnetic sample holder and measured in the RSO mode. The powdered sample **13** was placed in a quartz glass holder, fixed in a non-magnetic sample holder and measured in the DC mode. The magnetic data were corrected for the diamagnetic contribution of the sample holder and the quartz glass or gelatin capsule, respectively. The molar susceptibility data were corrected using the Pascal constant. The experimental data of **13** were fit assuming an $S = 0$ ground state and a temperature independent paramagnetism *TIP* due to Zeeman perturbation. The best fit for compound **13** was found with a paramagnetic impurity *PI* = 5.0 % per Cr ($S = 5/2$) and $TIP = 787 \cdot 10^{-6}$ $cm^3 \cdot mol^{-1}$.

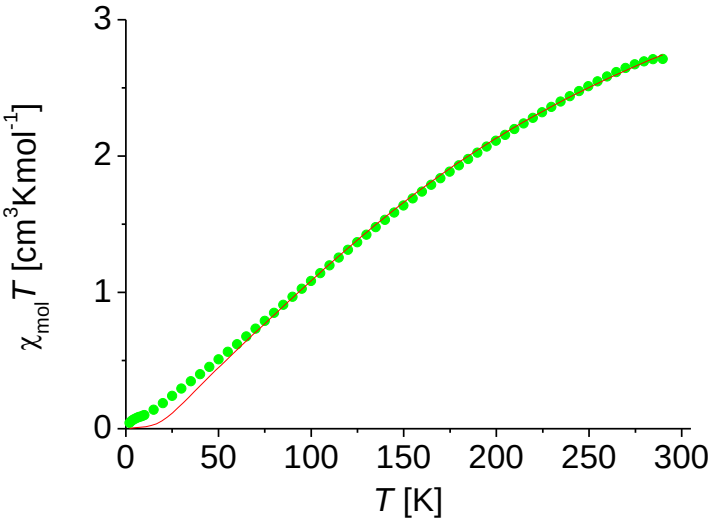

Figure S4. Temperature dependence of the $\chi_M T$ product of **12**. The solid line represents the fit with $H = -JS_1S_2$ (S = 3/2), J = -62 (1) cm^{-1} and TIP = 0.0013(1) $cm^3 \cdot mol^{-1}$ assuming g = 2.

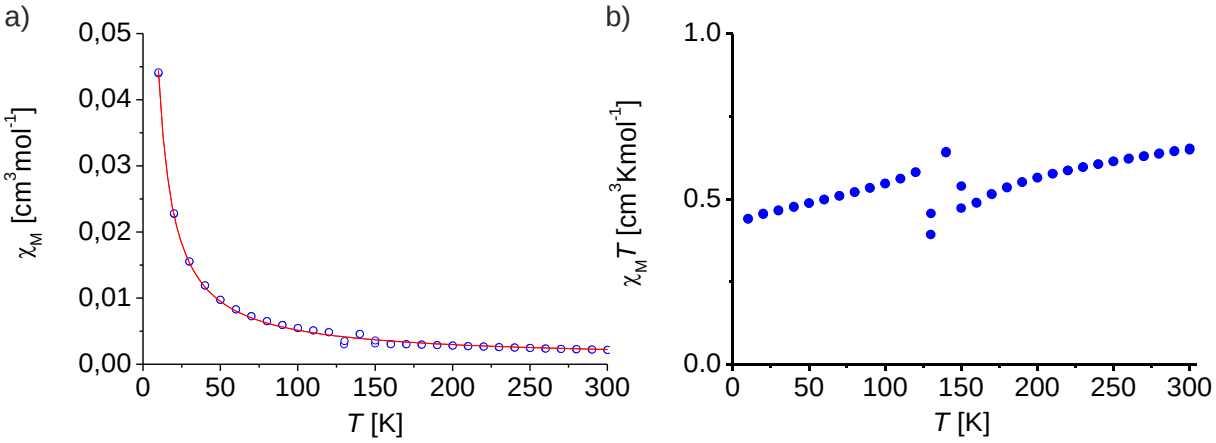

Figure S5. A) Temperature dependence of the molar susceptibility of **13** (open circles). The solid line reproduces the best fit with the parameters *PI* = 5.0 % per Cr (*S* = 5/2) and *TIP* = $787 \cdot 10^{-6}$ $cm^3 \cdot mol^{-1}$. B) Temperature dependence of the $\chi_M T$ product of **13**.

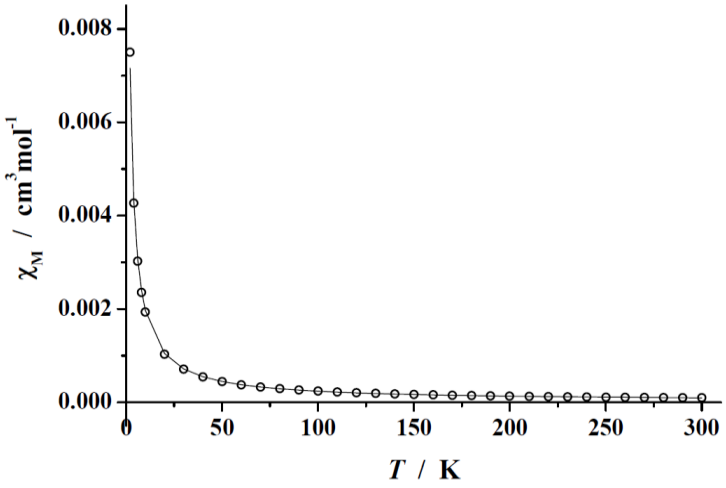

Figure S6. The temperature dependence of the molar magnetic susceptibility of **11**. The open points are the observed susceptibility, the black line reproduces the best fit with the parameters *PI* = 0.55 % (per Cr, *S* = 3/2 and Weiss constant θ = –1 K) and *TIP* = $26 \cdot 10^{-6}$ cm^3·mol^{-1}.

Computational details: Quantum chemical calculations were performed using the multi-configurational Complete Active Space SCF (CASSCF)[1] method, followed by second-order perturbation theory (CASPT2).[2] Relativistic all electron ANO-RCC basis sets with triple-zeta quality (ANO-RCC-VTZP) were used on chromium and nitrogen[3] and minimal basis sets (ANO-RCC-MB) on carbon and hydrogen.[4] Scalar relativistic effects were included using the Douglas-Kroll-Hess Hamiltonian.[5] The computational costs arising from the two-electron integrals were drastically reduced by employing the Cholesky decomposition (CD) technique[6] combined with the Local Exchange (LK) screening.[9] In the CASSCF treatment, the complete active space contains ten electrons in twelve active orbitals (10/12). This space comprises all 3d and 4s orbitals forming the Cr-Cr bond, namely one 4sσ, one 3dσ, two 3dπ and two 3dδ bonding and the corresponding antibonding orbitals. In the subsequent CASPT2 calculations, orbitals up to and including the 2p for Cr and 1s for C and N were kept frozen. The Frozen Natural Orbital approach with 70% of the virtual orbitals taken into account was applied to CASPT2 (FNO-CASPT2) for saving disk requirements and reducing computational costs.[10] C_i symmetry was imposed. The Cr-Cr bonding is quantified in terms of effective bond order (EBO), defined as $(\eta_b - \eta_a)/(\eta_b+\eta_a)$, where η_b is the occupation number for the bonding natural orbital andη_a is the occupation number for the corresponding antibonding natural orbital. The CASSCF/CASPT2 approach has proven to be very successful in the studies of metal-metal bonded compounds.[11,14] All calculations were performed with the MOLCAS 7.4 package.[15]

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5 Synthesis and Structure of Aminopyridinato and Guanidinato Ligand Stabilized Al-H Complexes

Tobias Bauer,[a] Winfried P. Kretschmer,[a] Muhammad Hafeez[a,b], and Rhett Kempe*[a]

[a] T. Bauer, Dr. W. P. Kretschmer, Dr. M. Hafeez, Prof. Dr. R. Kempe, Lehrstuhl Anorganische Chemie II, Universität Bayreuth, Universitätsstrasse 30, NW I, 95440 Bayreuth (Germany), Fax: (+49) 921552157, E-mail: kempe@uni-bayreuth.de

[b] Dr. M. Hafeez, Department of Chemistry, University of Azad Jammu and Kashmir, Muzaffarabad 13100, Azad Kashmir,(Pakistan).

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Keywords: Alanes•σ-alanes • N-ligands

Abstract: The reaction of the aminopyridine *N*-(2,6-di*iso*propylphenyl)-6-(pyrrolidin-1-yl)pyridin-2-amine (PyApH) and the guanidine *N,N*'-bis(2,6-di*iso*propylphenyl)piperidine-1-carboximidamide (PipGuH) with (freshly prepared) AlH_3 was investigated. For both N-ligands the formation of a dimeric, double hydrogen bridged aluminum dihydride complex is observed. The aminopyridinate is unstable and an intramolecular ligand redistribution reaction leading to monomeric $[(PyAp)_2AlH]$ is observed. The formation proceeds (most likely) via AlH_3 formation and its decomposition to Al and H_2. The guanidinate was found to be more stable and no ligand transfer was observed up to 50°C. Furthermore, the reaction of (2R,6S,*Z*)-*N,N'*-bis(2,6-di*iso*propylphenyl)-2,6-dimethylpiperidine-1-carboximidamide (MPipGuH) with $LiAlH_4$ was examined. The σ-alane lithium complex $[(MPipGu)(H)_2Al(\mu\text{-}H)Li(thf)_3]$ was formed in 81 % yield. It could be a suitable educt to synthesize other (for instance) σ-alane transition metal complexes.

5.1 Introduction

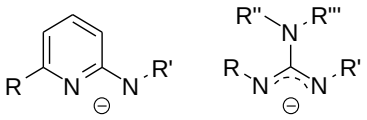
Aluminum is the third most abundant element and the most abundant metal in the earth`s crust. It`s hydride, alane, is prominently used in organic synthesis as reducing agent.[1] Moreover, it can be used to reduce metal complexes.[2] Furthermore, alanes have interesting applications in hydroalumination reactions[3], as precursors in metal organic chemical vapour

deposition,[4] and as hydrogen storage materials.[5,6] In addition, transition metal σ-alane complexes are of great interest.[7] Novel alanes could extent or improve these potential applications.

Herein we report on synthesis and structure of aminopyridinato and guanidinato ligand stabilized Al-H complexes. All complexes presented herein were characterized via single crystal X-ray structure analysis (XRD). Until now, only a small number of structurally fully characterized amidinato and guanidinato ligand stabilized alanes are known. Recently, a guanidinato ligand stabilized adduct of dialane (Al_2H_4) with an aluminum-aluminum bond was reported.[8]

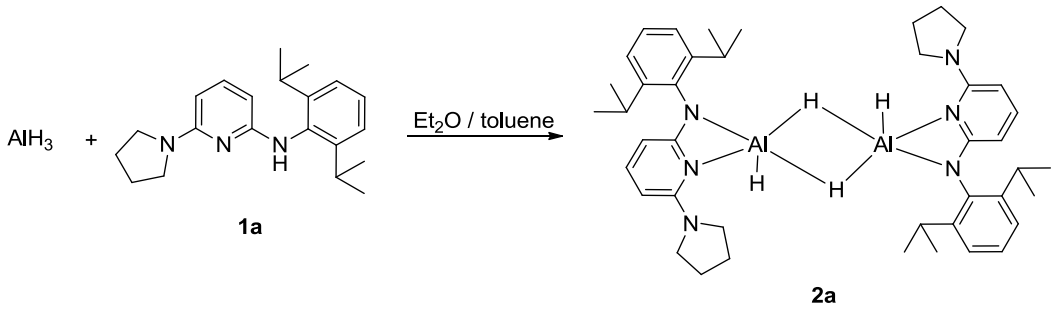
5.2 Results and Discussion

Aminopyridinato ligands (Ap, Scheme 1, left)[9,10,11] are bidentate, monoanionic ligands related to guanidinato ligands (Gu, Scheme 1, right)[12]. Both ligand classes are able to stabilize a broad variety of metal ions.[12,13]



Scheme 1. Aminopyridinato ligands and the related guanidinato ligands (R, R', R'', R''' = aryl, alkyl or silyl substituents).

As one can see, both ligand families can be fine-tuned with regard to their electron donating abilities and the steric bulk via the substituents (R and R' in the Ap system, R, R', R'' and R''' in the Gu system). Firstly, we started with studies on Ap ligand stabilized alanes. We did chose *N*-(2,6-di*iso*propylphenyl)-6-(pyrrolidin-1-yl)pyridin-2-amine (PyApH, **1a**) due to its electron donating ability.[14] Treatment of one equivalent of the aminopyridine **1a** in toluene with one equivalent of in situ prepared AlH_3 in a 1:2 mixture of ether/toluene lead to the formation of the dimeric aluminium hydride species $[(PyApAlH_2)_2]$ **2a** in 54% yield (Scheme 3). Crystals suitable for XRD analysis could be grown by storage of a concentrated toluene solution of **2a** at -40°C. The molecular structure of compound **2a** is shown in Figure 1.Experimental details of the XRD studies can be found in Table 1. NMR studies of compound **2a** revealed, as expected, a single set of proton resonances for the equivalent Ap ligands and a very broad singlet at δ = 5.00 ppm for the four aluminium hydrides. This indicates fluxional, dynamic behaviour in solution.



Scheme 3. Synthesis of the dimeric compound **2a.**

Two doublets at δ = 5.07 and 5.19 ppm belonging to the aromatic protons in the pyridine ring (3 and 5 position) are quite up field for aromatic protons. This can be explained by the increased electron donating ability of the PyAp ligand due to the pyrolidinyl moiety. Another confirmation for the increased electron donating ability of PyAp is found in the crystal structure of **2a**. The sum of all angles around N3 is 359.8°, indicating a nearly perfect planar sp^2 hybridized N atom. The torsion angle by which N3 is shifted out of the plane is only 2.7°. Moreover, the distance between N3 and C5 is 1.3475(10) Å, lying between a N-Csp^2 double bond (1.28 Å in average) and a N-Csp^2 single bond (1.48 Å in average).[15] The amido N-Al distance of 1.8742(6) Å and the pyridine N atom to Al distance of 2.0358(7) Å indicate that the anionic charge of the Ap ligand is localized at the amido N atom. The aluminum centers are five-coordinated by two N atoms (from the Ap ligand), a terminal and two bridging hydrides.

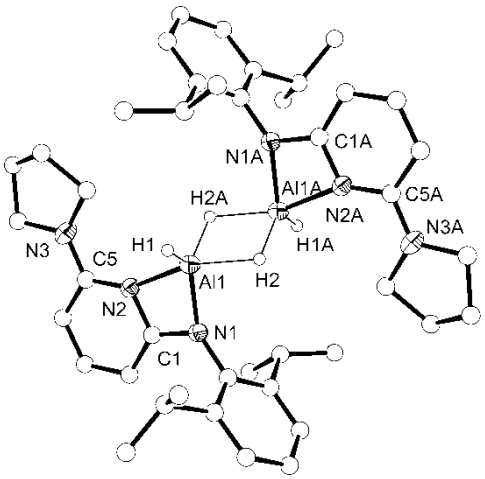
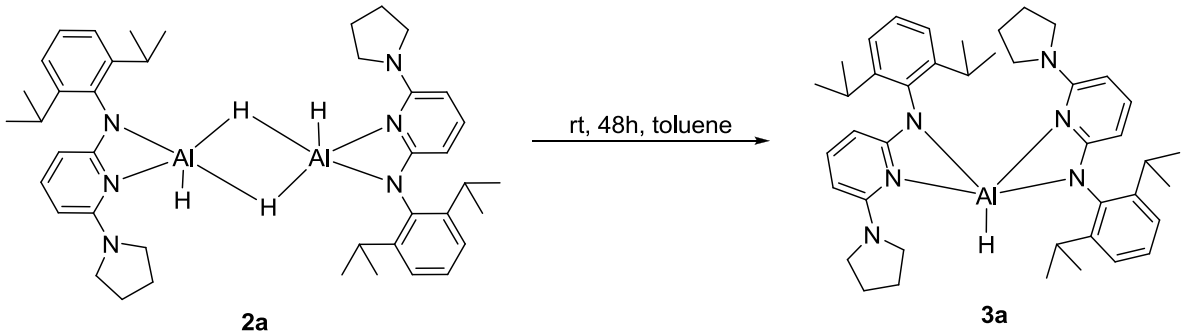


Figure 1. Molecular structure of compound **2a** with 50% thermal ellipsoids. Carbon atoms are displayed as spheres, Hydrogen atoms, except of the hydrides, are omitted for clarity. Selected bond lengths [Å] and bond angles [°]:Al1–H1 1.479(9), Al1–H2 1.624(9), C5–N3 1.3475(10), C5–N2 1.3498(10), N1–Al1 1.8742(6), N2–Al1 2.0358(7), N1–C1–N2 107.53(6).

The bridging hydrides where found to have bond lengths of 1.624(9) Å (Al1–H2) and the terminal ones of 1.479(9) Å (Al1–H1). Cole *et al.*,[16] reported on a amidinato ligand stabilized alane [{(Piso)Al(H)(μ-H)}$_2$] (Piso = ArNC(*t*Bu)NAr, Ar = 2,6-di*iso*propyl-phenyl) having bond lengths to the aluminum center of 1.64(2) Å for the bridging hydrides and of 1.51(3) Å for the terminal ones. Frenking, Jones, Stasch and co-workers[8] reported on [{(Priso)Al(H)(μ-H)}$_2$] (Priso = ArNC(R)NAr, Ar = 2,6-di*iso*propyl-phenyl, R = N*iso*Propyl$_2$). Their hydrides have bond lengths to Al of 1.60(2) Å (bridging) and 1.54(3) Å (terminal). Quantum chemical calculations done by Himmel[17] suggest this type of structural motif for N-ligands bearing high steric bulk. If a solution of **2a** is kept at room temperature for two days a metal like precipitate is formed. Furthermore, H_2 was observed in the ^{1}H NMR spectra of a solution of **2a** kept for two days at room temperature. The decomposition of non solvated alane into the elements is documented.[18] Filtration and concentration of the filtrate gave colorless crystals suitable for XRD analysis in 65% isolated Yield. The XRD study revealed a monomeric species, namely (PyAp)$_2$AlH (**3a**, Figure 2). This finding indicates that Ap ligand redistribution takes place.[19] Compound **3a** shows proton resonances one would expect for non mirror symmetric bis(Ap) complexes. The aluminum hydride resonance could not be assigned. Most likely it lies underneath the proton resonances found for the methyl groups in the ligands *iso*propyl moieties.[20]



Scheme 4. Formation of compound **3a.**

The molecular structure of **3a** shows similar structural parameters for the Ap ligand as in compound **2a**. The bond length Al1–H1 1.52(2) Å lies in between the bond distances found for the hydrides in compound **2a** (1.624(9) and 1.479(9) Å, respectively). Teuben and co-workers reported on [{PhC(NSiMe$_3$)$_2$}$_2$AlH],[20] the first complex with this structural motif. In this complex, an Al–H distance of 1.55(2) Å was observed.

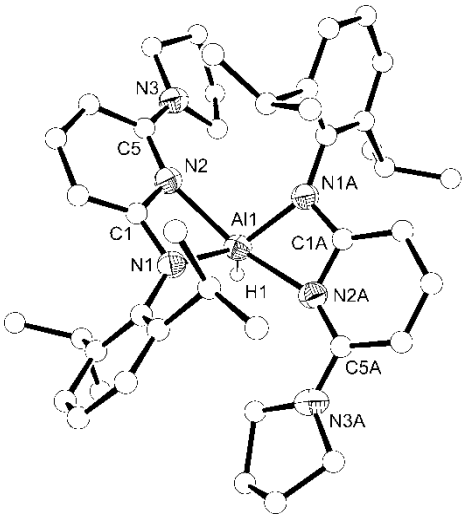
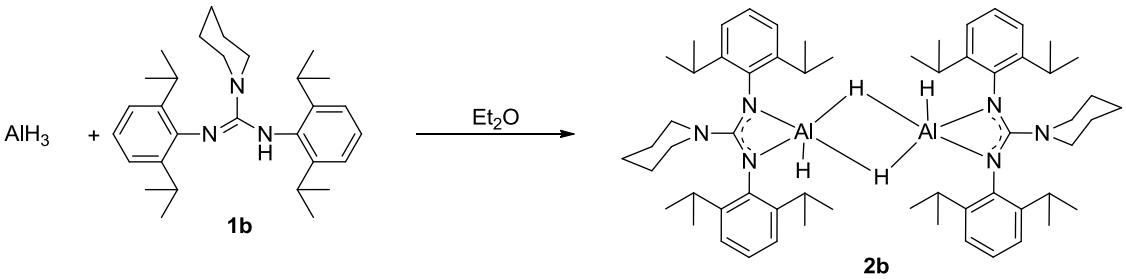


Figure 2. Crystal structure of compound **3a** with 50% thermal ellipsoids. Carbon atoms are displayed as spheres, Hydrogen atoms, except of the hydride, are omitted for clarity. Selected bond lengths [Å] and bond angles [°]:Al1–H1 1.52(2), C5–N3 1.348(3), C5A–N3A 1.346(3), N1–Al1 1.8881(19), N2–Al1 2.1213(19), N1A–Al1 1.8821(19), N2A–Al1 2.1308(19), N1–C1–N2 108.74(19), N1A–C1A–N2A 108.55(19).

Theoretical work[17] showed, that five-coordinated aluminum hydride complexes stabilized by two amidinato ligands are highly stable. In order to obtain thermally more robust Al dihydride complexes we used sterically demanding Gu ligands. Based on our recent findings, guanidinato ligands are less prone to ligand transfer reaction pathways.[14,21] The reaction of equimolar quantities of *N,N*'-bis(2,6-di*iso*propylphenyl)piperidine-1-carboximidamide (PipGuH, **1b**) with freshly prepared AlH_3 in ether led, after removing all volatiles, to a spectroscopically pure colorless solid of compound **2b** (Scheme 4) in nearly quantitative yield. Recrystallization at -40°C afforded colorless cube like crystals in 87% isolated yield.



Scheme 4. Synthesis of the dimeric compound **2b**.

NMR studies showed one set of proton signals for the Gu ligands and again a very broad singlet at δ= 4.83 ppm for the four aluminum hydrides. A slight upfield shift of the hydride resonances in comparison to **2a** (δ = 5.00 ppm) is observed. XRD analysis revealed a dimeric structure of **2b** (Figure 3) comparable to that of **2a**. The found Al–H distances are 1.424(17) for the terminal

(Al1–H1) and 1.575(18) Å for the bridging hydride (Al1–H2). They are significantly shorter than the ones in **2a** (1.479(9) and 1.624(9) Å, respectively). Thermal treatment (50°C) of **2b** for over two days showed no signs of ligand distribution in the ^{1}H-NMR spectra.

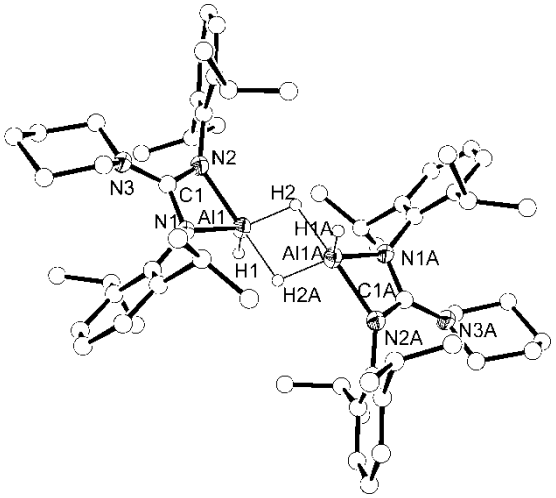
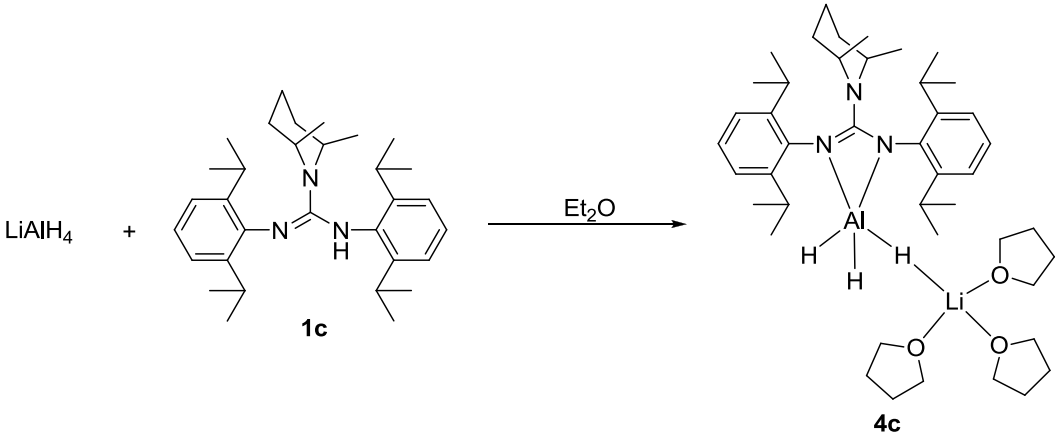


Figure 3. Molecular structure of **2b** with 50% thermal ellipsoids. Carbon atoms are displayed as spheres, Hydrogen atoms, except of the hydrides, are omitted for clarity. Selected bond lengths [Å] and bond angles [°]:Al1–H1 1.424(17), Al1–H2 1.575(18), C1–N3 1.3543(17), N1–Al1 1.9792(12), N2–Al1 1.9159(11), N1–C1–N2 109.12(11).

Inspired by the stability of **2b**, we used an even bulkier Gu ligand namely (2R,6S,Z)-*N,N'*-bis(2,6-di*iso*propylphenyl)-2,6-dimethylpiperidine-1-carboximidamide (MPipGuH) to synthesize a "monomeric" σ-alane lithium complex. Reaction of lithiumalanate with one equivalent of MPipGuH (**1c**) in ether leads to formation of an off-white precipitate. Workup by filtration and removing all volatiles under reduced pressure gave a spectroscopically pure colorless powder of compound **4c** (Scheme 5) in nearly quantitative yield. Crystallization from a concentrated THF solution at -40°C afforded colorless crystals suitable for XRD study (Yield: 81%). The molecular structure of compound **4c** is depicted in Figure 4.



Scheme 5. Synthesis of the guanidinato ligand stabilized σ-alane lithium complex**4c**

NMR studies revealed a set of proton signals for the Gu ligand and a very broad singlet in the range δ = 3.6-4.3 ppm integrating to three protons for the aluminum hydrides. This indicates dynamic behavior of the hydrides in solution within the time regime of NMR spectroscopy. In the solid state, a monomeric compound with a unique structural motif is revealed. The Al center is five-coordinated with the Gu ligand bound in a *N,N'*-dihapto-chelating mode. Two terminal hydrides and a bridging hydride to a THF stabilized Li atom accomplish the coordination sphere around the Al atom.

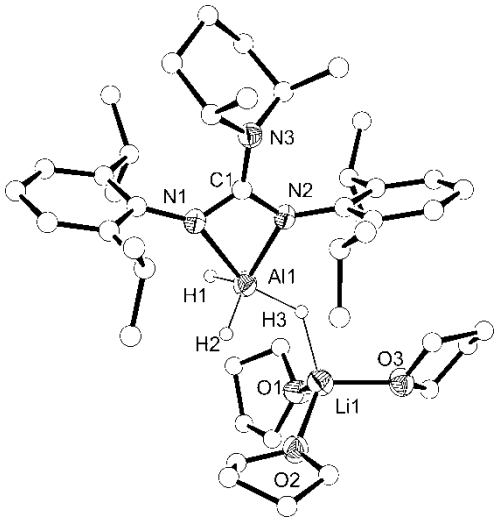


Figure 4. Crystal structure of compound **4c** with 50% thermal ellipsoids. Carbon atoms are displayed as spheres, Hydrogen atoms, except of the hydrides, are omitted for clarity. Selected bond lengths [Å] and bond angles [°]:Al1–H1 1.521(19), Al1–H2 1.500(19), Al1–H3 1.622(18), Li1–H3 1.815(18), C1–N3 1.3831(18), N1–Al1 2.2388(12), N2–Al1 1.9331(12), Li1–O (average value) 1.954; N1–C1–N2 109.83(12).

The bond distances of the hydrides to the central aluminum atom are Al1–H1 1.521(19), Al1–H2 1.500(19) and Al1–H3 1.622(18) Å. The bond length between Li1 and H3 is 1.815(18) Å. These values are comparable to previously reported Al–H and bridging Li–H–Al interactions.[22] A comparable amidinato stabilized aluminum hydride is reported by Cole *et al.*,[16] namely the dimeric compound [{(μ-Fiso)Al(H)(μ-H)$_2$Li(OEt$_2$)}$_2$]. There, the Fiso ligand adopts a bridging mode, rather than a chelating mode like in compound **4c**, bridging the Al and Li centers. Due to inter- and intramolecular Al–H–Li bridges an eight membered $Li_2Al_2H_4$ ring is observed. The bridging Al–H distances of 1.51(3) and 1.56(3) Å are shorter than the one found in compound **4c** (1.622(18) Å). The terminal Al–H distance of 1.52(3) Å is in total agreement with our finding and the Li–H distance of 1.93(3) is a little longer than the one in **4c** (1.815(18) Å).

5.3 Conclusions

In conclusion, molecular aluminum hydrides stabilized by either aminopyridinato or guanidinato ligands were synthesized. For the used Ap ligand, it was found that the formed dimeric (double hydrogen bridge) dihydride complex is thermally unstable. A ligand redistribution reaction led to a monohydride and alane at room temperature. The related, isostructural Gu complex proves to be stable even at elevated temperatures (50°C). An even bulkier Gu ligand gave rise to a unique aluminum hydride complex with an Al–H–Li bridge (σ-alane complex of lithium). It might be a suitable educt to synthesize σ-alane complexes of other metals via Li salt elimination.

Table 1: Details of the X-ray crystal structure analyses.

Compound	***2a***	***3a***	***2b***	***4c***
Crystal system	triclinic	triclinic	monoclinic	triclinic
space group	*P*-1	*P*-1	$P2_1/n$	*P*-1
a [Å]	9.0860(7)	13.3410(5)	9.7810(5)	12.5760(6)
b [Å]	9.3390(7)	16.1430(6)	18.5670(8)	12.9720(6)
c [Å]	13.0020(9)	17.8240(6)	16.1030(7)	15.6160(7)
α [°]	93.149(6)	85.241(3)	90.000	92.030(4)
β[°]	101.877(6)	89.706(3)	98.207(4)	96.047(4)
γ [°]	112.140(6)	88.410(3)	90.000	114.109(3)
V [Å^3]	989.30(13)	3823.9(2)	2894.4(2)	2303.72(18)
Z	1	4	2	2
ρ(calcd.) [gcm^{-3}]	1.180	1.169	1.092	1.049
μ (mm^{-1})	0.111	0.091	0.091	0.082
T [K]	133	133	133	133
2*θ* range [°]	4.76-56.35	2.53-55.00	3.37-56.35	2.63-56.23
Reflections unique	21924	16636	6776	10758
Refl. obsv. [$I > 2\sigma(I)$]	17526	10877	5674	7968
Parameters	239	944	334	501
R_1, wR_2 [$I > 2\sigma(I)$]	0.0440, 0.1176	0.0560, 0.1553	0.0467, 0.1139	0.0490, 0.1312
R_1, wR_2 *(all data)*	0.0550, 0.1221	0.0884, 0.1662	0.0593, 0.1201	0.0683, 0.1384

5.4 Experimental Section

General: All manipulations were performed with rigorous exclusion of oxygen and moisture in Schlenk-type glassware on a dual manifold Schlenk line or in an N_2 filled glove box (mBraun 120-G) with a high-capacity recirculator (<0.1ppm O_2). Solvents were dried by distillation from sodium wire/benzophenone. Commercial $AlCl_3$ (Sigma-Aldrich) and $LiAlH_4$ (Merck) was used as received. PyApH[14a], AlH_3[18], PipGuH[23] and MPipGuH[24] were prepared according to published procedures. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were degassed, dried and distilled prior to use. NMR spectra were recorded on Varian Unity 300 MHz and Varian Unity 400 MHz instruments at ambient temperature. The chemical shifts are reported in ppm relative to the internal TMS or residual solvent signals. Elemental analyses (CHN) were determined using a Vario EL III instrument. X-ray crystal structure analyses were performed by using a STOE-IPDS II equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement was accomplished using SIR97,[25] SHELXL97[26] and WinGX.[27]

Synthesis of [{(PyAp)Al(H)(μ-H)}$_2$] (2a):

PyApH (0.646 g, 2 mmol) in toluene (5 mL) was slowly added with a syringe to a freshly prepared solution of AlH_3 in a 1:2 mixture of ether/toluene (15 mL, 2 mmol) at 0° C. After stirring at this temperature for 1h, the reaction mixture was concentrated and stored overnight at -40°C to give **2a** as colorless crystals. Yield: 0.380 g (54 %). $C_{42}H_{60}Al_2N_6$ (702.93): Calcd. C 71.76, H 8.60, N 11.96; found. C 71.20, H 9.01, N 11.71;^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 1.17 (m, 8H,C*H*$_2$), 1.25 (d, 12H, J_{HH} = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.40 (d, 12H, J_{HH} = 6.8 Hz, CH(C*H*$_3$)$_2$), 2.97 (m, br, 8H, C*H*$_2$), 3.75 (sept, 4H, J_{HH} = 6.8 Hz, C*H*(CH$_3$)$_2$), 5.00 (s, br, 4H, Al*H*), 5.07 (d, 2H, J_{HH} = 8.1 Hz, C*H*), 5.19 (d, 2H, J_{HH} = 7.8 Hz, C*H*), 6.88 (t, 2H, J_{HH} = 8.1 Hz, C*H*), 7.23 (s, br, 6H, arom-H), ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 24.82, 24.88, 25.02, 28.73, 47.09, 90,86, 93,64, 123.81, 125,97, 138,51, 142.15, 146.78, 154.10, 165.74.

[(PyAp)$_2$AlH] (3a):

A freshly prepared solution of AlH_3 in ether (15 mL, 2 mmol) was slowly treated with PyApH (0.646 g, 2 mmol) in ether (5 mL) via addition with a syringe at 0°C. This reaction mixture was stirred for 48h at ambient temperature leading to a metallic grey precipitate. After filtration and concentration of the reaction mixture colorless crystals of **3a** can be isolated. Yield: 0.436 g (65 %). $C_{42}H_{57}AlN_6$ (672.92): Calcd. C 74.96, H 8.54, N 12.49; found. C 74.54, H 8.91, N 12.36, ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 1.03 (d, 6H, J_{HH} = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.13 (m, 8H, C*H*2), 1.23 (d, 6H, J_{HH} = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.26 (d, 6H, J_{HH} = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.28 (d, 6H, J_{HH} =

6.8 Hz, CH(CH_3)$_2$), 2.63 (m, 4H, CH_2), 3.02 (m, 4H, CH_2), 3.59 (sept., 2H, CH(CH$_3$)$_2$), 3.65 (sept., 2H, CH(CH$_3$)$_2$), 5.21 (d, 2H, J_{HH} = 7.7 Hz, m-$C_5N_1H_3$), 5.27 (d, 2H, J_{HH} = 7.7 Hz, m-$C_5N_1H_3$), 6.94 (t, J_{HH} = 8.0 Hz, 2H, p- $C_5N_1H_3$), 7.10-7.19 (m, 6H, arom. CH). ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 22.09, 24.65, 25.04, 25.17, 27.22, 28.41, 28.94, 45.13, 46.94, 91.85, 93.91, 123.27, 124.30, 125.66, 127.70, 140.27, 140.87, 146.67, 147.53, 154.86, 166.71.

Synthesis of [{(PipGu)Al(H)(μ-H)}$_2$] (2b):

To a freshly prepared solution of AlH_3 in ether (15 mL, 2 mmol) was added a solution of PipGuH (895.4 mg, 2 mmol) in ether (10 mL). The reaction mixture was stirred at 300 rpm over night. Concentration of the mixture to approximately 5 mL, followed by heating until the saturated solution started to boil, gave colorless crystals suitable for X-ray structure analysis upon storage at ambient temperature. Yield: 0.828 g (87 %). $C_{60}H_{92}Al_2N_6$ (951.38): Calcd. C 75.75, H 9.75, N 8.83; found. C 75.30, H 9.61, N 8.78; ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 0.83 (m, br., 12H CH_2), 1.29 (d, 24H, CH(CH_3)$_2$), 1.34 (d, 24H, CH(CH_3)$_2$), 2.73 (m, 8H, N(CH_2)$_2$), 3.68 (sept, 8H, CH(CH$_3$)$_2$), 4.83 (s, br, 4H Al-H), 7.07 – 7.11 (m, 12H, m-C_5H_3, p-C_5H_3). ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 23.23, 23.49, 24.78, 26.12, 28.47, 47.67, 105.19, 123.88, 139.12, 144.53, 163.67.

Synthesis of [(MPipGu)(H)$_2$Al(μ-H)Li(thf)$_3$](4c):

$LiAlH_4$ (151.8 mg, 4 mmol) was dissolved in ether (10 mL) at 0° C and MPipGuH (1.902 g, 4 mmol) in ether (10 mL) was added slowly. The reaction mixture was allowed to warm to ambient temperature and was stirred at 300 rpm overnight. The solvent was removed under reduced pressure and the crude residue was extracted with THF. Concentration of the clear solution gave colorless crystals after storage at 10° C overnight. Yield: 2.359 g (81 %). $C_{44}H_{75}AlLiN_3O_3$ (728.01): Calcd. C 72.59, H 10.38, N 5.77; found. C 72.92, H 10.82, N 6.55; ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 0.77 (d, 6H, J_{HH} = 7.0 Hz, N{CH(CH_3)}$_2$),0.86-1.23 (m, 6H, CH2), 1.32 (m, br, 12H, THF), 1.37 (d, 12H, J_{HH} = 6.8 Hz, CH(CH_3)$_2$), 1.41 (d, 12H, J_{HH} = 6.8 Hz, CH(CH_3)$_2$), 3.43 (m, 12H, THF),3.6-4.3 (m, br, 3H. Al-H), 3.81 (sept., 4H, CH(CH$_3$)$_2$), CH(CH$_3$)$_2$), 3.93 (sept., 2H, NCH(CH$_3$)), 7.02-7.19 (m, 6H, arom. CH). ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 13.65, 21.37, 23.31, 25.56, 26.94, 28.46, 29.78, 48.43, 123.72, 145.08, 163.40.

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6 Synthesis and Structure of a Trinuclear Yttrium Polyhydride Cluster Stabilized by a Bulky Guanidinato Ligand

Tobias Bauer[a], and Rhett Kempe*[a]

[a] T. Bauer, Prof. Dr. R. Kempe, Lehrstuhl Anorganische Chemie II, Universität Bayreuth, Universitätsstrasse 30, NW I, 95440 Bayreuth (Germany), Fax: (+49) 921552157, E-Mail: kempe@uni-bayreuth.de

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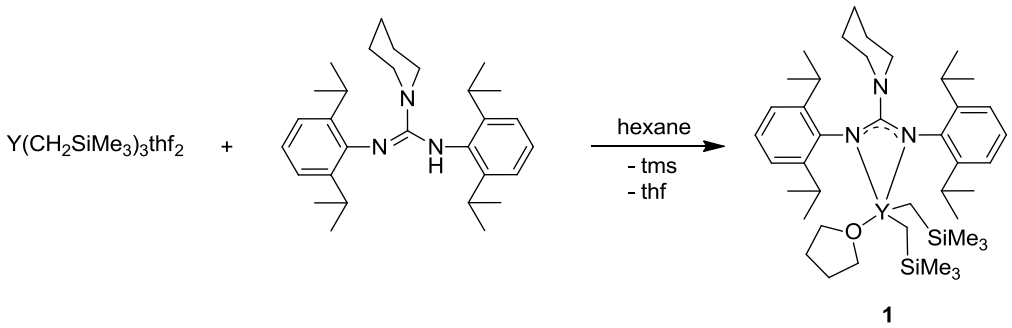
6.1 Introduction

Polyhydride complexes of the rare earth (RE) metals (group 3 metals and lanthanoid metals [Ce-Lu]) have fascinated chemists due to their reactivity and structural motifs. Furthermore, RE (poly)hydrides are among the most reactive compounds known.[1] Recently, the interest in RE hydrides has shifted from monohydride L_2LnH complexes[2] to dihydride $LLnH_2$ complexes. The dihydride complexes tend to aggregate and vary in structure ranging from hexanuclear,[1e,3a-c] pentanuclear,[3c] tetranuclear,[3b-j,3o] trinuclear[3b,3k-o] to dinuclear complexes.[3r] The nuclearity mainly dependents from the steric bulk of the ancillary ligand used. An increase in the steric demand of the ancillary ligand seems to lead to a decrease in nuclearity. Structurally fully characterized (trustable determination of the positions of the hydrogen atoms) lanthanide polyhydride complexes still lack in number. Until now, mostly sterically demanding cyclopentadienyl derivatives,[3d-h,3j] scorpionato [tris(pyrazolyl)hydroborate] ligands,[3a,b] tetraazacycloamido[3l] and aminopyridinato ligands[3m,q] have been used to stabilize the "$(LnH_2)_x$" unit.

Herein, we report on synthesis and structure of the first RE $(LnH_2)_3$ polyhydride stabilized by a guanidinato ligand.

6.2 Results and Discussion

All complexes synthesized were characterized by NMR spectroscopy, elemental analysis and single crystal X-ray structure analysis (XRD). First, we synthesized the guanidinate yttrium dialkyl complex **1** (Scheme 1). The equimolar reaction of thf stabilized yttrium trialkyl ($Y(CH_2SiMe_3)_3thf_2$) with the guanidine (*Z*)-*N,N'*-bis(2,6-di*iso*propylphenyl)piperidine-1-carboximidamide (PipGuH) in *n*-hexane afforded clean formation of the guanidinato ligand stabilized yttrium dialkyl complex [PipGuY$(CH_2SiMe_3)_2$thf] **1** in 80 % yield (Scheme 1). NMR investigation of compound **1** showed, as one would expect for a mononuclear complex, a single set of proton resonances for the guanidinato ligand, one signal set for the two alkyl moieties and one signal set for the coordinated thf. The YCH_2 resonance (D_6-benzene, rt) for **1** is found at δ = -0.26 ppm with a coupling constant J_{YH} = 3.0 Hz. This is in good comparison to related NMR studies (D_6-benzene, rt) on guanidinato ligand stabilized yttrium dialkyl [(ArNC(NMe2)NAr)Y$(CH_2SiMe_3)_2$thf][4] (δ = -0.31, J_{YH} = 2.9 Hz), amidinato ligand stabilized yttrium dialkyl [PhC-$(NAr)_2$]Y$(CH_2SiMe_3)_2$thf][5] (δ = -0.11, J_{YH} = 3 Hz) and aminopyridinato ligand stabilized yttrium dialkyl [(Ar)6-{(2,4,6-tri*iso*propylphenyl) pyridine-2-yl)amido}Y$(CH_2SiMe_3)_2$thf][6] (δ = -0.42 J_{YH} = 3.0 Hz) (Ar = 2,6-di*iso*propylphenyl) complexes.



1

Scheme 1. Synthesis of **1**.

Single crystals suitable for XRD analysis were grown from a saturated hexane/toluene (1:1 ratio) solution by slowly cooling to -40° C. The molecular structure of compound **1** is depicted in Figure 1. Compound **1** crystallizes in the monoclinic spacegroup *P*2(1)/n and features a *N,N'*-dihapto-guanidinato ligand, two alkyl moieties and one thf molecule coordinated to the Y atom. The O atom of the thf molecule occupies a position roughly in the plane defined by the central yttrium atom and the two nitrogen atoms of the guanidinato ligand. To minimize steric repulsion with the ligand 2,6-diisopropylphenyl groups, the two alkyl moieties occupy positions above and below this plane. The bond lengths from the central yttrium atom to the ligand nitrogen atoms are 2.349(2) and 2.335(2) Å. In comparison to the related complex reported by Hessen and co-workers [(ArNC(NMe2)NAr)Y$(CH_2SiMe_3)_2$thf][4]

(Ar = 2,6-di*iso*propylphenyl) the found C–Y bond distances of 2.378(3) and 2.391(3) Å in compound **1** are slightly longer than the ones in the Hessen compound (2.374(4) and 2.384(4) Å).

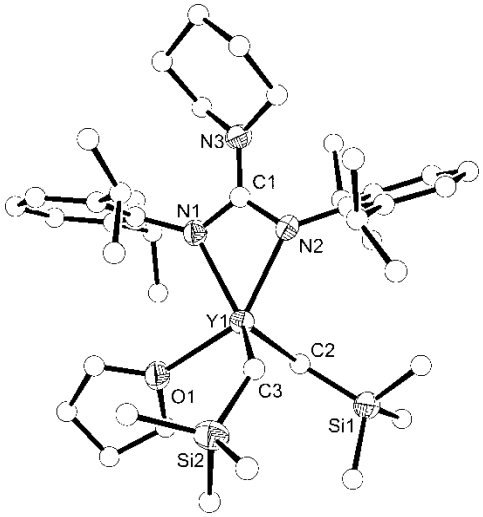
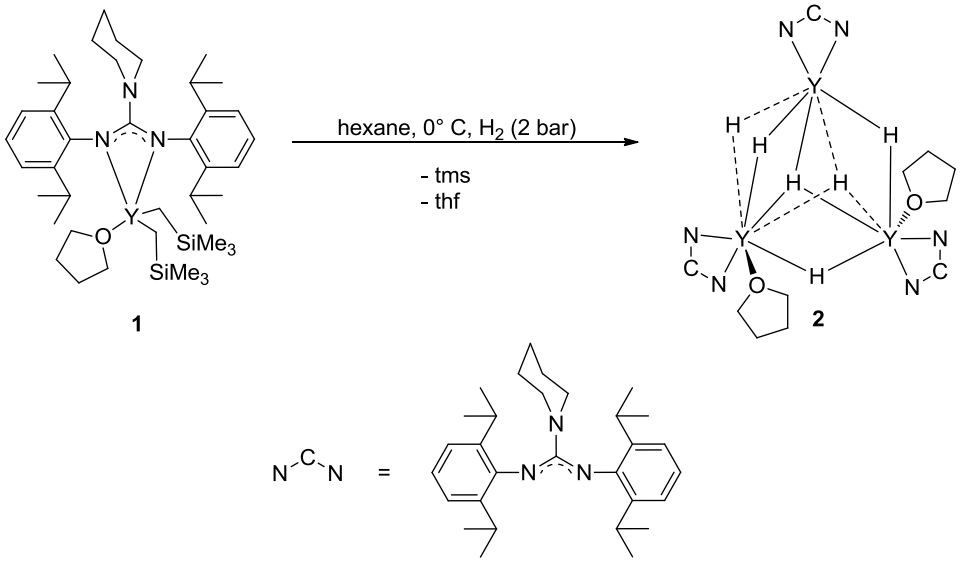


Figure 1. Molecular structure of compound **1**. Ellipsoids are drawn on the 50 % probability level. Carbon atoms are shown as spheres and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]:C2–Y1 2.378(3), C3–Y1 2.391(3), C1–N1 1.346(4), C1–N2 1.350(4), C1–N3 1.366(4), N1–Y1 2.349(2), N2–Y1 2.335(2), O1–Y1 2.382(2), N1 C1 N2 111.9(3).

Hydrogenolysis of compound **1** at 0°C (2 bar H_2 pressure) afforded clean formation of the trinuclear polyhydride complex [{(PipGu)YH_2}$_3$thf$_2$] (**2**, Scheme 2) as indicated by the NMR studies and XRD analysis.



Scheme 2. Synthesis of **2**.

^{1}H NMR investigations of compound **2**, in contrast to the studies of compound **1**, gave rather broad resonance peaks of the three guanidinato ligands, the two coordinated thf molecules and a sharp quartet for the six hydrides (J_{YH} = 18.5 Hz). In solution, we face a complex dynamic behavior. The three guanidinato ligands are not equivalent which can be explained by the fact, that two of the three yttrium centers have a coordinated thf molecule and therefore the rotation in two of the three ligands is hindered at room temperature. All six hydrides give rise to a single quartet at δ = 6.26 ppm due to coupling with the three yttrium atoms. This shows that the hydrides, in solution, are all equivalent and very fluxional in the time scale of NMR spectroscopy and are not distinguishable like in the solid-state structure. Reports on other trinuclear yttrium hexahydride complexes are in agreement with our finding.[3b,p,l] To get a deeper insight into the dynamic behavior of compound **2** we carried out variable temperature ^{1}H NMR studies (Figure 2). Upon heating to 100°C the three guanidinato ligands give rise to a single set of proton resonances as can be seen in Figure 2 B). This confirmed that the broadening of the ligand signals are due to hindrance in rotation at room temperature and/or an equilibrium in coordination and decoordination of thf. The quartet at δ = 6.26 ppm shows peak broadening down to -35°C. At this temperature, the hydrides start to become inequivalent and their fast skipping is hindered as seen in Figure 2 C). Unfortunately, the limiting spectra where the μ_3- and μ_2-hydrides become distinguishable could not be obtained.

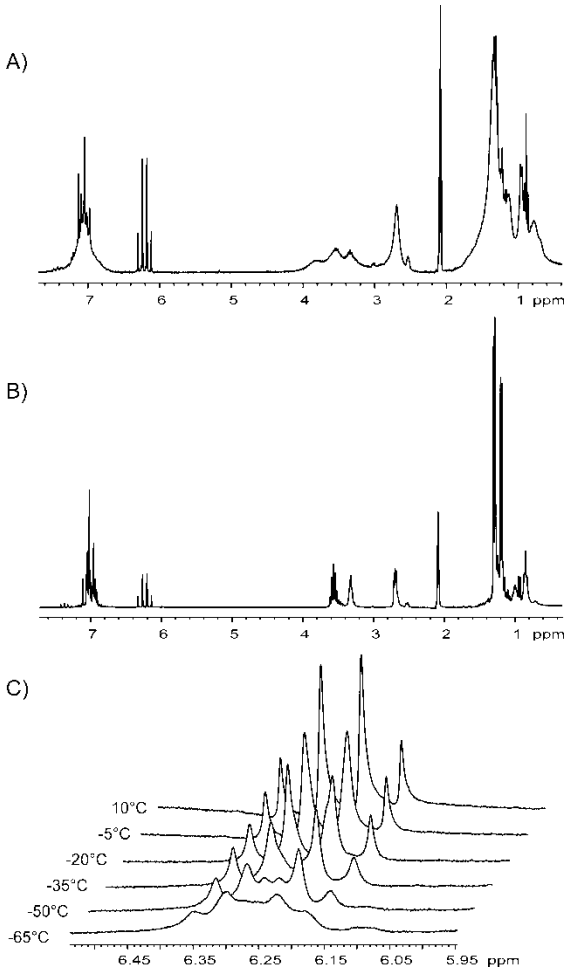


Figure 2. A) ^{1}H NMR spectrum of **2** (D_8-toluene, rt, 7.6 to 0.4 ppm). B) ^{1}H high temperature NMR spectra of **2** (D_8-toluene, 100°C, 7.6 to 0.4 ppm). C) ^{1}H variable low temperature NMR spectra of **2** (D_8-toluene, -65 to 10°C, 6.50 to 5.95 ppm).

A molecular structure of compound **2** is depicted in Figure 3 and a more detailed view of the core structure with peripheral ligands reduced is shown in Figure 4. Selected interatomic distances and bond lengths are summarized in Table 1. Details on the XRD analysis of compound **1** and **2** are given in Table 2.

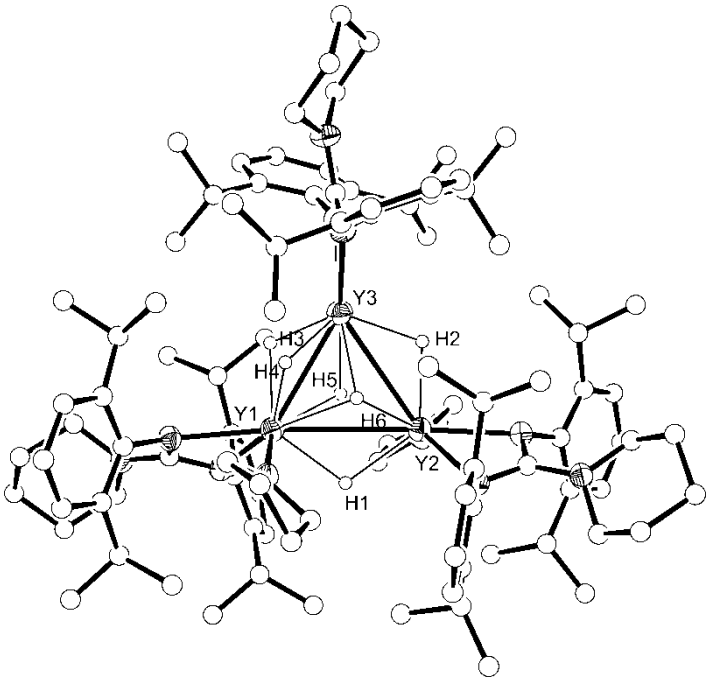


Figure 3. Molecular structure of compound **2**. Ellipsoids are drawn on the 50 % probability level. Carbon atoms are shown as spheres and non hydride hydrogen atoms are omitted for clarity.

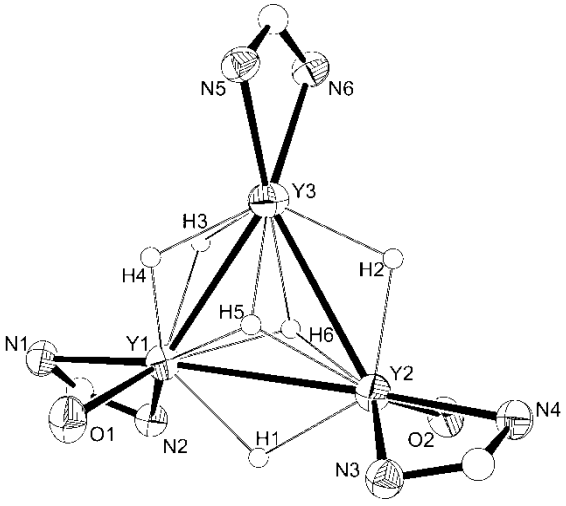


Figure 4. Detailed view of the cluster core with peripheral ligands drawn as NCN moieties and thf molecules as O atoms.

Table 1. Selected interatomic distances and bond lengths [Å] of compound **2**.

N–Y (average value)	2.387
O–Y (average value)	2.362
Y(1,2,3)–H5	2.22(4), 2.16(4), 2.12(4)
Y(1,2,3)–H6	2.11(4), 2.11(4), 2.24(4)
Y(1,2)–H1	2.20(4), 2.17(4)
Y(2,3)–H2	2.09(4), 2.17(4)
Y(1,3)–H3	2.14(4), 1.93(3)
Y(1,3)–H4	2.01(4), 2.04(4)
Y1–Y2	3.5457(6)
Y1–Y3	3.1697(5)
Y2–Y3	3.4293(6)

Compound **2** crystalizes in the monoclinic spacegroup *P*2(1)/c with a *n*-hexane molecule per asymmetric unit. Each Y atom in complex **2** bears a guanidinato ligand in the same *N,N'*-dihapto mode like in the precursor complex **1** but with longer Y-N distances due to higher coordination number of the yttrium atoms. The three yttrium atoms define a triangle. Four of the six hydride ligands bridge one of the three Y---Y edges in a μ_2 mode, meaning one of the edges is bridged by two μ_2-hydrides while the other two edges are bridged by only one μ_2-hydride. The last two hydrides are capping the sides of the Y_3 plane in a μ_3 fashion. The Y---Y edge bridged by two hydrides is significantly shorter than the two other edges (3.1697(5) Å in comparison to 3.4293(6) and 3.5457(6) Å, respectively). This Y---Y distance is the second shortest ever reported, the shortest being 3.1648(7) Å reported by Hou and co-workers.[3p] Other $(YH_2)_3$ cluster compounds have Y-H and Y---Y distances in the range from 2.06(4) to 2.37(4) Å and 3.1648(7) to 3.6841(2) Å.[3b,p,l]

Table 2. Details of the X-ray crystal structure analyses.

Compound	***1***	***2***
Crystal system	monoclinic	monoclinic
space group	*P*2(1)/n	$P2_1/c$
a [Å]	13.9090(5)	13.4210(5)
b [Å]	19.5700(7)	17.3420(6)
c [Å]	16.9340(6)	44.0040(16)
α [°]	90.00	90.00
β[°]	98.455(3)	97.532(3)
γ [°]	90.00	90.00
V [Å^3]	4559.3(3)	10153.4(6)
Z	4	4
ρ (calcd.) [g cm^{-3}]	1.139	1.206
μ [mm^{-1}]	1.363	1.751
T [K]	133	133
2*θ* range [°]	2.43-54.09	2.53-54.97
Reflections unique	9716	21989
Refl. obsv. [$I > 2\sigma(I)$]	4784	9777
Parameters	466	1083
R_1, wR_2 [$I > 2\sigma(I)$]	0.0415, 0.0649	0.0464, 0.0812
R_1, wR_2 *(all data)*	0.1082, 0.0769	0.1259, 0.0983

6.3 Conclusions

In conclusion, we have synthesized a guanidinato ligand stabilized $(YH_2)_3$ polyhydride complex starting from the corresponding guanidinato ligand stabilized yttrium dialkyl complex. This could be achieved via hydrogenolysis of the dialkyl complex and followed aggregation of three (YH_2) units to form the corresponding trinuclear yttrium hexahydride complex. We could show that the used guanidinato ligand PipGu can stabilize yttrium alkyl and yttrium hydride species. Variable temperature ^{1}H NMR studies on the polyhydride complex **2** showed a highly

dynamic behavior. Reactivity studies on this polyhydride to form heteromultimetallic polyhydride complexes are under way.

6.4 Acknowledgments

Financial support by the Deutsche Forschungsgemeinschaft (DFG, KE 756/ 21-1) is gratefully acknowledged.

6.5 Experimental Section

General: All manipulations were performed with rigorous exclusion of oxygen and moisture in Schlenk-type glassware on a dual manifold Schlenk line or in an N_2 filled glove box (mBraun 120-G) with a high-capacity recirculator (<0.1ppm O_2). Solvents were dried by distillation from sodium wire/benzophenone. PipGuH,[7] and $Y(CH_2SiMe_3)_2thf_2$[8] were prepared according to published procedures. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were degassed, dried and distilled prior to use. NMR spectra were recorded on Varian Unity 300 MHz and Varian Unity 400 MHz instruments at ambient temperature. The chemical shifts are reported in ppm relative to the internal TMS or residual solvent signals. Elemental analyses (CHN) were determined using a Vario EL III instrument. X-ray crystal structure analyses were performed by using a STOE-IPDS II equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement was accomplished using SIR97,[9]SHELXL97[10] and WinGX.[11]

Synthesis of [PipGuY($CH_2SiMe_3)_2$thf] (1):

To a solution of $Y(CH_2SiMe_3)_3thf_2$ (2 mmol, 0.990 g) in hexane (15 mL) at 0°C was slowly added a solution of PipGuH (2 mmol, 0.895 g) in hexane (10 mL). The reaction mixture was allowed to slowly get to room temperature within one hour and was kept at this temperature over night. All volatiles where removed under reduced pressure and an off-white powder of compound **1** was isolated in nearly quantitative yield. Recrystallization from a concentrated hexane/toluene solution and storage at -40° C gave colorless cube like crystals (1.250 g, 1.6 mmol, 80 % yield) suitable for XRD analysis.$C_{42}H_{74}N_3OSi_2Y$ (782.13): Calcd. C 64.50, H 9.54, N 5.37; found. C 64,23, H 9.71, N 5.42, ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = -0.26 (d, 4H, J_{YH} = 3 Hz, CH_2SiMe_3), 0.27 (s, 18H, $CH_2Si\mathit{Me}_3$), 0.82 (m, br, 4H, CH_2), 0.92 (m, br, 2H. CH_2), 1.19, (m, br, 4H, THF), 1.33 (d, 12H, J_{HH} = 6.8 Hz, $CH(CH_3)_2$), 1.43 (d, 12H, J_{HH} = 6.8 Hz, $CH(CH_3)_2$), 2.75 (m, br, 4H, $N(CH_2)_2$), 3.58 (m, br, 4H, THF), 3.67 (sept. 4H, J_{HH} = 6.8 Hz, $CH(CH_3)_2$), 7.05-7.18

(m, 6H, arom. C*H*) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 4.39, 23.73, 23.94, 24.70, 24.94, 26.43, 28.15, 38.30 (d, J_{YC} = 40.7 Hz), 48.15, 70.56, 124.06, 142.37, 144.12, 165.83 ppm.

Synthesis of [(PipGuYH$_2$)$_3$thf$_2$] (2):

In the glovebox, a pressure tube equipped with a magnetic stirring bar and a valve was charged with a solution of compound **1** (0.75 mmol, 0.587 g) in hexane (15 mL). The tube was sealed and transferred out of the glovebox and cooled to 0°C. The tube was then pressurized with H_2 to 2 bar and stirred for 24h at this temperature. The tube was returned to the glovebox, pressure was released and the reaction mixture was filtered to a Schlenk type glass tube. Outside the glovebox all volatiles where removed under vacuum to give an off-white powder of compound **2** (0.421 g, 0.72 mmol, 96 % yield). Crystals suitable for XRD analysis were grown by slowly cooling a concentrated, boiling hexane solution to room temperature.$C_{98}H_{154}N_9O_2Y_3 \cdot C_6H_{14}$(1757.05·86.18): Calcd. C 67.77, H 9.19, N 6.84; found. C 67.18, H 8.84, N 6.97¸ ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 0.80 (m, br, 12H, CH_2), 0.94 (m, br, 6H. CH_2), 1.22, (m, br, 8H, THF), 1.37 (m, br 72H, CH(CH_3)$_2$), 1.43 (d, 12H, J_{HH} = 6.8 Hz, CH(CH_3)$_2$), 2.73 (m, br, 12H, N(CH_2)$_2$), 3.10 – 4.10 (m, br, 28H, THF, CH(CH$_3$)$_2$), 6.26 (quart., 6H, J_{YH} = 18.5 Hz, Y-*H*) 7.01-7.35 (m, 18H, arom. C*H*) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 23.69, 23.73, 24.27, 24.92, 25.57, 27.81, 28.72, 29.06, 48.92, 70.86 (br), 123.17, 123.69, 142.75, 145.98, 166.67 ppm.

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7 Ternary Rare-Earth Transition-Metal Polyhydride Cluster Compounds

Tobias Bauer,[a] Frank R. Wagner*[b], and Rhett Kempe*[a]

Dedicated to Werner Uhl on the occasion of his 60th birthday

[a] T. Bauer, Prof. Dr. R. Kempe, Lehrstuhl Anorganische Chemie II, Universität Bayreuth, Universitätsstrasse 30, NW I, 95440 Bayreuth (Germany), Fax: (+49) 921552157, E-Mail: kempe@uni-bayreuth.de

[b] Dr. F. R. Wagner, Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Str. 40, 01187 Dresden (Germany), Fax: (+49) 351-4646-4002, E-Mail: wagner@cpfs.mpg.de

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7.1 Introduction

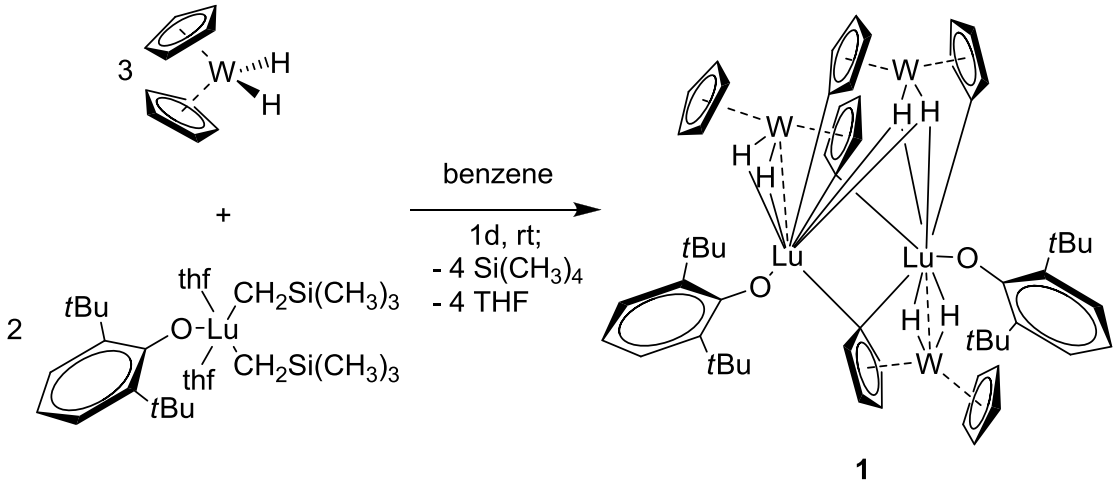
Many important catalytic cycles or selective stoichiometric transformations rely on metal hydrides as key intermediates.[1] The reactivity of rare earth (RE) metal hydrides differ drastically from that of the late transition metals (TM). The former preferably undergo σ-bond metathesis reactions, whereas the latter are prone to oxidative addition, as well as reductive elimination steps. In consequence, heteromultimetallic polyhydride complexes composed of RE metals and (late) TM are of great interest due to expected synergistic effects of the different metal centers. RE–TM hydride (intermetallic compounds) are applied as hydrogen storage materials[2] or in car batteries,[3] and the molecular analogues are interesting alternatives for these applications. In addition, they are interesting model systems for the intermetallic RE–TM hydride compounds.[4] The first studies on RE–TM polyhydride complexes date back nearly 30 years.[5] Despite the many years of research, only a rather small number of RE–TM polyhydride complexes are known. Reasons are most likely the lack of efficient synthesis protocols and difficulties in terms of characterization of such compounds. Handling and storage are problematic due to the high sensitivity/reactivity. Furthermore, the paramagnetism of most of the RE metals restricts studies

by NMR spectroscopy. Finally, XRD studies are challenging due to poor/difficult localization of the hydrides next to the electron-rich and heavy diffracting RE (and TM) atoms.[6] To date, heteromultimetallic complexes with bridging hydride ligands to support the RE–TM interaction have been prepared by salt elimination,[7] H_2 elimination,[8] alkane elimination,[9] and C–H bond activation.[10] Furthermore, the class of compounds has been extended to RE–main group metal polyhydrides.[11]

Herein we report the synthesis and (electronic) structure of new RE–TM polyhydrides, especially the first examples of ternary polyhydrides. These polyhydrides also feature RE–TM bonds. RE–TM bonding has received a lot of attention recently.[9c,12,13]

7.2 Results and Discussion

The reaction of one and a half equivalents of $[Cp_2WH_2]$ (Cp = cyclopentadienyl) with $[Lu(OAr)R_2(thf)_2]$ (ArO = 2,6-di-*tert*-butyl-phenolate, R = $CH_2Si(CH_3)_3$) in benzene at room temperature gave the heteromultimetallic polyhydride cluster compound **1** in 75% yield (Scheme 1). The compound showed poor solubility in aromatic solvents and is insoluble in aliphatic hydrocarbons. This cluster features three tungsten centers and two lutetium centers as shown by X-ray crystal structure analysis (Figure 1). Each lutetium atom has the coordination number nine containing one phenolato ligand, three C–H activated Cp rings, two μ_3-hydrido ligands and two tungsten metals bridged by two μ_2-hydrides.



Scheme 1: Synthesis of **1**.

The Lu–W distances of 3.1211(10) Å and 3.1155(9) Å are shorter than the sum of the covalent radii of Lu and W (3.49 Å) based on data reported by Alvarez and co-workers[14] and are in good agreement with the sum of the atomic radii in crystals for Lu and W (3.1 Å) based

on report of Slater.[15] ^{1}H NMR studies at room temperature showed singlets in the hydride region with a 2:1 ratio for the six hydride ligands in compound **1** at δ = –13.69 (4H, J_{WH} = 83.3 Hz) and –13.27 ppm (2H, J_{WH} = 104.1 Hz). These signals show an upfield shift in comparison to the signal at –12.26 ppm for the educt [Cp_2WH_2]. The observed J_{WH} coupling constant of 83.3 Hz is greater than that for [Cp_2WH_2] of 73.0 Hz. The same effect was reported for the comparable compounds [$Cp^*_2Y(\mu\text{-}\eta^1\text{:}\eta^5\text{-}C_5H_4)(\mu\text{-}H)_2WCp$] ($J_{WH}$ = 78.0 Hz, Cp* = pentamethylcyclopentadienyl)[8a] and [$(Et_3P)_2(H)Ir(\mu\text{-}\eta^1\text{:}\eta^5\text{-}C_5H_4)H_2WCp$] with J_{WH} coupling constants of 92.4 Hz and 95.2 Hz.[16] The second J_{WH} coupling constant of 104.1 Hz is even greater and might indicate that the hydride ligands on the bridging tungstenocene moiety are bound in a μ_3-fashion by W3, Lu1 and Lu2. The C–H activated Cp ligands showed signals that one would expect for a mirror symmetric C_5H_4 moiety with two singlets per activated Cp ligand giving three sets of signals in a 2:1:1 ratio.

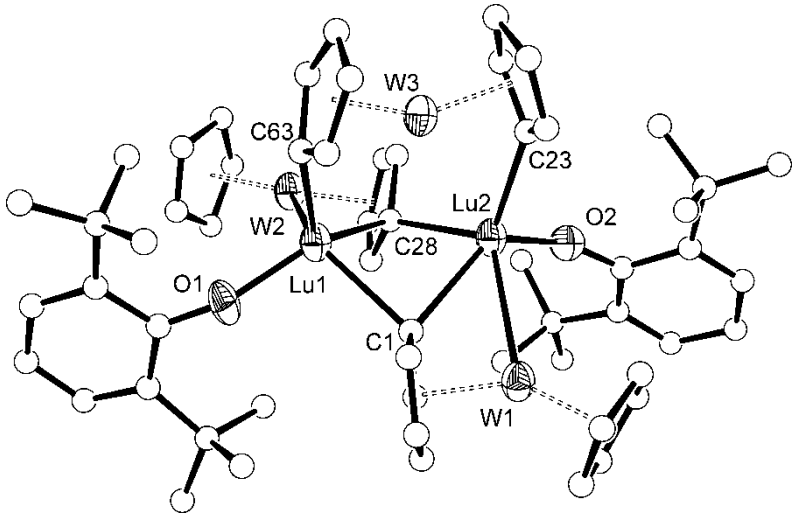
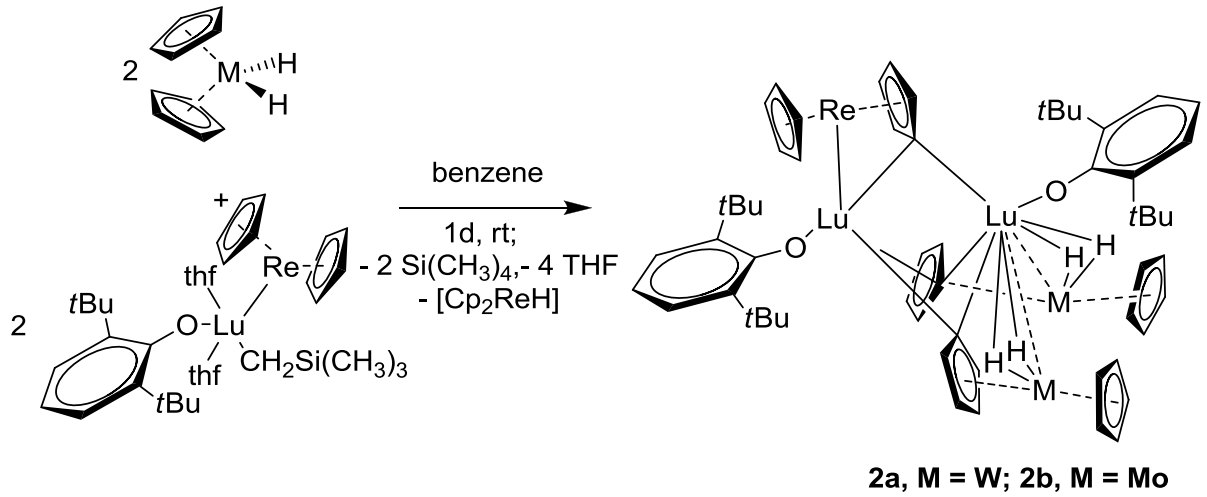


Figure 1. ORTEP drawing of compound **1** with 50% thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å]: Lu1–O1 2.107(11), Lu2–O2 2.081(10), Lu1–W2 3.1211(10), Lu2–W1 3.1155(9), Lu1–C1 2.485(14), Lu2–C1 2.558(14), Lu1–C28 2.554(14), Lu2–C28 2.493(15), Lu1–C63 2.366(17), Lu2–C23 2.315(17), $Cp_{centroid}$–W1 1.965, $C_5H_{4centroid}$–W1 1.927, $Cp_{centroid}$–W2 1.954, $C_5H_{4centroid}$–W2 1.935, $C_5H_{4centroid}$–W3 1.932 (average value).

The selective cluster formation via C–H bond activation indicative by the good isolated yield of **1** inspired us to investigate the formation of ternary polyhydride clusters. We chose [Lu(OAr)(Cp_2Re)R(thf)] as a promising and rather reactive educt (Scheme 2).[13c] Reacting equimolar amounts of [Lu(OAr)(Cp_2Re)R(thf)] with [Cp_2WH_2] in benzene at room temperature lead to the formation of the trimetallic polyhydride cluster compound **2a** in 48% yield (Scheme 2). To the best of our knowledge, compound **2a** is the first example of a RE-metal polyhydride cluster featuring three different metals as was revealed by XRD and NMR studies (Figure 2).

Compound **2a** is well soluble in aromatic solvents and shows no solubility in aliphatic hydrocarbons.



Scheme 2: Synthesis of **2a** and **2b**.

One of the lutetium centers in **2a** is five coordinate by one phenolato ligand, three C–H activated Cp rings, and a rhenium atom. The other lutetium center has the coordination number ten containing a phenolato ligand, three C–H activated Cp ligands, and two tungsten atoms each bridged by two μ_2-hydrides.

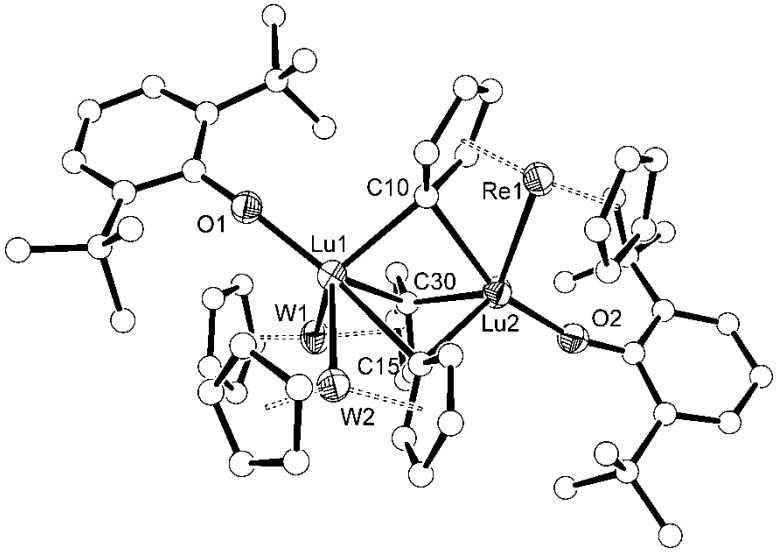


Figure 2.ORTEP drawing of **2a** with 50% thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å]: Lu1–O1 2.109(5), Lu2–O2 2.082(5), Lu1–W1 3.1760(5), Lu1–W2 3.2033(5), Lu2–Re1 2.7986(5), Lu1–C10 2.434(8), Lu1–C15 2.608(8), Lu1–C30 2.543(9), Lu2–C10 2.464(7), Lu2–C15 2.440(8), Lu2–C30 2.430(8), $Cp_{centroid}$–W1 1.889, $C_5H_{4centroid}$–W1 1.867, $Cp_{centroid}$–W2 1.984, $C_5H_{4centroid}$–W2 1.918, $Cp_{centroid}$–Re1 1.869, $C_5H_{4centroid}$–Re1 1.857.

The Lu–Re bond distance is 2.7986(5) Å, which is way shorter than the sum of the covalent radii of rhenium and lutetium (3.38 Å) based on Alvarez and co-workers data,[14] shorter

than the sum of the atomic radii in crystals (3.1 Å) based on Slater,[15] and even shorter than the bond lengths in [Lu($Cp_2Re)_3$] (2.8773(8), 2.8899(7) and 2.8913(8) Å)[13c] and in [Lu(OAr)($ReCp_2$)R(thf)] (2.8498(6) Å).[13e] The Lu–W bond lengths are 3.1760(5) and 3.2033(5) Å. As such, they are longer than in **1,** but still shorter than the sum of the covalent radii[14] and the sum of the atomic radii.[15] The hydride signals in the ^{1}H NMR spectrum of compound **2a** are shifted upfield again to δ = –13.61 ppm and show a J_{WH} coupling constant of 82.5 Hz which is in good agreement with the finding for compound **1** (J_{WH} = 83.3 Hz). There are no further hydride signals present indicating a non hydride-bridged Lu–Re bond. Each of the phenolato ligands shows one set of signals at room temperature.

Finally, we became interested in synthesizing the molybdenum analogue of **2a**. The equimolar reaction of [Cp_2MoH_2] with [Lu(OAr)(Cp_2Re)R(thf)] in benzene gave the isostructural heteromultimetallic polyhydride cluster **2b** in 52% yield (Figure 3 and Scheme 2). The Lu–Mo bond distances of 3.2025(12) and 3.1613(9) Å are shorter than the sum of the covalent radii of 3.41 Å based on report of Alvarez and co-workers,[14] and in good agreement with the sum of the atomic radii of 3.2 Å based on report of Slater.[15] Again, an upfield shift of the singlet at δ = –10.25 ppm accounting for four hydride protons can be seen in the ^{1}H NMR spectrum, recorded at room temperature, in comparison to the singlet at δ = –8.80 ppm for the hydrides in [Cp_2MoH_2].

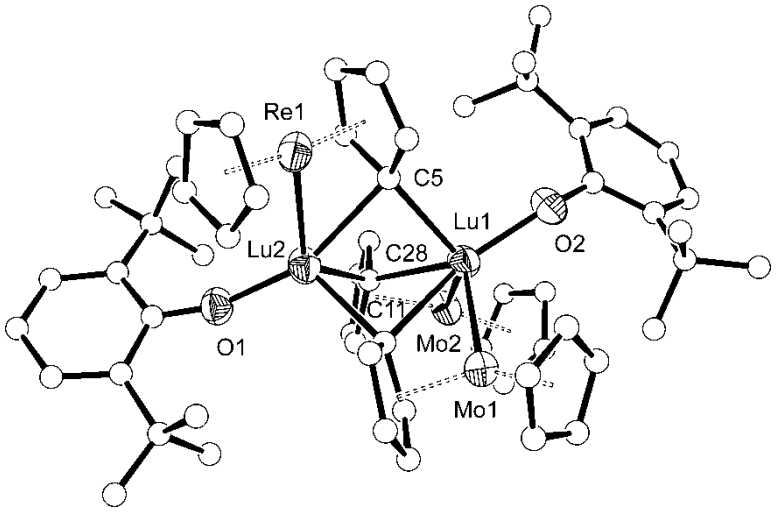


Figure 3.ORTEP drawing of **2b** with 50% thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å]: Lu1–O1 2.111(7), Lu2–O2 2.074(7), Lu1–Mo1 3.2025(12), Lu1–Mo2 3.1613(9), Lu2–Re1 2.8058(6), Lu1–C5 2.412(10), Lu1–C11 2.608(13), Lu1–C28 2.591(12), Lu2–C5 2.484(10), Lu2–C11 2.403(12), Lu2–C28 2.426(11), $Cp_{centroid}$–Mo1 1.982, $C_5H_{4centroid}$–Mo1 1.917, $Cp_{centroid}$–Mo2 1.965, $C_5H_{4centroid}$–Mo2 1.888, $Cp_{centroid}$–Re1 1.879, $C_5H_{4centroid}$–Re1 1.852.

Quantum chemical calculations were performed to locate the missing hydride-atomic positions in compound **2a** and to analyze their role in W–Lu bonding compared to Re–Lu

bonding in the cluster compounds **2**. For that purpose, full structure optimization has been invoked on a slightly simplified model structure **2a'** (substituting H for the *tert*-butyl groups) for compound **2a**. For the scalar-relativistic (ZORA approach)[17] calculations with the ADF[18] program system the DFT/BP86[19] method and internal Slater-type triple-zeta basis sets with two sets of polarization functions ("TZ2P", with frozen small core) have been employed. After 100 optimization cycles the –OPhen groups were fixed, and the remaining atom positions were further optimized. At gradients of less than 0.3 mHartree$Å^{-1}$, the procedure was finished. The final structure, especially the inner metal part, is very similar to the one from experimental structure determination.

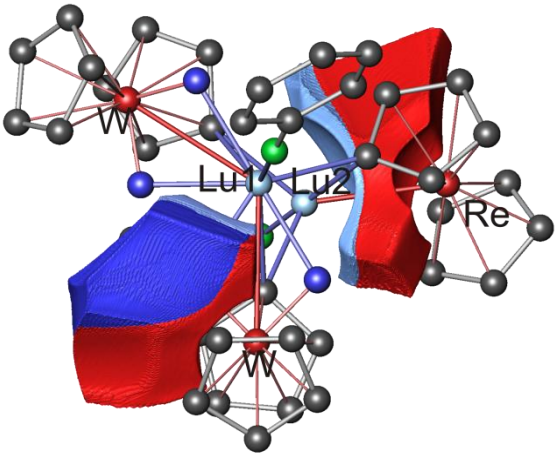


Figure 4. Optimized structure of model **2a'** with ELI-D/QTAIM basin intersections. Hydridic H atoms are displayed as blue spheres, intersection of corresponding ELI-D basin yields a region (deep blue) contained in the QTAIM H atom, a region (red) contained in the W QTAIM atom, and a region (light blue) contained in Lu1 atom; intersection of the ELI-D Lu-Re bond basins yields a region (red) belonging to the Re atom, and a region (light blue) belonging to the Lu2 atom; all basins are cropped at density values below 0.0001 e/$Bohr^{-3}$.

It displays distances *d*(Lu1–W) of 3.13 and 3.14 Å (vs. 3.18 and 3.20 Å from experimental structure determination), *d*(Lu2–Re1) = 2.81 Å (vs. 2.80 Å from experiment), and *d*(W–H) between 1.72 and 1.73 Å with angles H-W-H of 87.3° and 87.6°. Under the same computational conditions a separate structure optimization of the [Cp_2WH_2] molecule yields *d*(W–H) = 1.71 Å and angle H-W-H = 78.6°, which shows that the distances W–H only marginally increase upon coordination to Lu, whereas the angle H-W-H notably widens by 9°. Concerning the electronic structure, a HOMO-LUMO gap of 1.5 eV is found, in which the HOMO, HOMO-1 and HOMO-2 can be classified as nominal Re(5d) orbitals. As has been previously done,[9c, 13c,d,e] position-space bonding analysis (program DGrid[20]) by using the electron density (QTAIM method)[21] and the electron localizability indicator (ELI-D)[22] has been employed. The negative values Q^{eff}(H) = –0.35 ±0.01 for the QTAIM effective charges of the

four W-H-Lu1 bridging H atoms was consistent with their hydridic character. These values were found to be very similar to the ones Q^{eff} (H) = –0.30 in the isolated [Cp_2WH_2] molecule. Applying the method of ELI-D/QTAIM basin intersection[23] yields that W–H bonding is polar-covalent with 70% of the ELI-D basin integrated charge density of each hydridic H atom belongs to the corresponding QTAIM H atom and 26% to the QTAIM W atom (Figure 4). Only a tiny amount of 3% is contained in the QTAIM Lu1 atom. Taking into account the positive effective charge Q^{eff} (Lu1) = +1.9, this finding is to be interpreted as a very ionic type of bonding interaction H–Lu1, which is consistent with the virtually unchanged distances *d*(W–H) compared to isolated [Cp_2WH_2]. Concerning direct W–Lu1 bonding a corresponding ELI-D maximum was not displayed; however owing to the bridging H atoms, this would not be expected to occur. As a signature of W–Lu1 bonding, inside the quadrilateral W-H'-Lu1-H'', a region with negative values of the Laplacian of ELI-D,[22c] which extends perpendicular to the W–Lu1 interconnection line, can be found. Such a region does not occur in the isolated molecule [Cp_2WH_2], but is found also for the Lu2–Re bonding situation, in which ELI-D attractors additionally signify the covalent bonding interaction. In complete analogy to previous cases of polar-covalent rare earth-transition metal bonding,[9c, 13,c,d,e] unsupported Lu2–Re bonding is indicated by corresponding ELI-D maxima with 1.30 electrons in two Lu2–Re bonding ELI-D basins (merged into one superbasin). The ELI-D/QTAIM intersection procedure showed that 79% of the basin population is contained in the Re, and 16% in the Lu QTAIM atom, which is similar to previous cases.

7.3 Conclusions

In conclusion, transition metal dihydride complexes of the formula [Cp_2MH_2] (M = Mo, W) react with rare earth metal bis- and monoalkyl complexes and undergo multiple C–H bond activation steps, leading to binary and ternary RE-metal polyhydride cluster compounds. The ternary clusters display polar Re→Lu bonds and W–H···Lu interactions, where the hydride atoms are polar-covalently coordinated to W, and the interaction with Lu is very ionic. Additionally, a covalent direct interaction W–Lu is indicated by ELI-D analysis. Concerning the broader strategy of building higher aggregated ternary RE–TM polyhydride clusters [Cp_2MH_2] represents a promising transition metal building block. In the future work, we are interested in studying the reactivity of the cluster compounds introduced herein.

7.4 Acknowledgments

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Supporting Information available: Supporting information for this article contains detailed information on the synthesis and characterization of the compounds described herein, as well as crystallographic details of the structures determined by XRD. It is available on the WWW under http://dx.doi.org/10.1002/chem.201301290.

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7.6 Supporting Information

7.7 General

All manipulations were performed with rigorous exclusion of oxygen and moisture in Schlenk-type glassware on a dual manifold Schlenk line or in a N_2 filled glove box (mBraun 120-G) with a high-capacity recirculator (<0.1ppm O_2). Solvents were dried by distillation from sodium wire/benzophenone. Commercial [Cp_2WH_2] (ABCR) was used as received. [$Lu(OAr)R_2(thf)_2$],[1] [$Lu(OAr)(ReCp_2)R(thf)$],[1] [Cp_2MoH_2][2] and [Cp_2ReH][3] were prepared according to published procedures. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were degassed, dried and distilled prior to use. NMR spectra were recorded on Varian Unity 300 MHz and Varian Unity 400 MHz instruments at ambient temperature. The chemical shifts are reported in ppm relative to the internal TMS or residual solvent signals. Elemental analyses (CHN) were determined using a Vario EL III instrument. X-ray crystal structure analyses were performed by using a STOE-IPDS II equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement was accomplished using SIR97,[4] SHELXL97[5] and WinGX.[6] Crystallographic details are summarized in Table 1. CCDC-932376 (for **1**), -932377 (for **2a**), and -932378 (for **2b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

7.8 Details of the X-ray crystal structure analyses

Table 1: Details of the X-ray crystal structure analyses.

Compound	***1***	***2a***	***2b***
Crystal system	triclinic	monoclinic	monoclinic
space group	*P*-1	$P2_1/c$	$P2_1/c$
a [Å]	14.5190(7)	19.4320(5)	19.2850(5)
b [Å]	14.5450(7)	18.5290(4)	18.1160(5)
c [Å]	16.5350(8)	19.4310(5)	19.4870(5)
α [°]	86.651(4)	90.00	90.00
β[°]	68.746(4)	119.476(2)	117.975(2)
γ [°]	76.211(4)	90.00	90.00
V [Å^3]	3159.0(3)	6090.7(3)	6012.6(3)
Z	2	4	4
ρ (calcd.) [g cm^{-3}]	1.950	2.026	1.859
μ [mm^{-1}]	8.580	8.999	5.709
T [K]	133	133	133
2θ range [°]	2.64-50.39	2.41-50.06	2.39-53.91
Reflections unique	10601	10239	12771
Refl. obsv. [$I > 2\sigma(I)$]	5588	7554	7715
Parameters	709	706	640
R_1, wR_2 [$I > 2\sigma(I)$]	0.0506, 0.1134	0.0336, 0.0703	0.0555, 0.1348
R_1, wR_2 *(all data)*	0.0935, 0.1217	0.0526, 0.0741	0.0929, 0.1474

7.9 Synthesis and characterization of the cluster compounds

Synthesis of $[C_{58}H_{74}Lu_2O_2W_3]$ (1):

$[Cp_2WH_2]$(71 mg, 225 µmol) was dissolved in benzene (1.5 mL) and added to a solution of $[Lu(OAr)R_2(thf)_2]$ (105 mg, 150 µmol) in benzene (1.5 mL). The reaction mixture was kept at room temperature for 24 hours without stirring to form a yellow crystalline precipitate. Yield: 0.096 g, 75%. Yellow prism like crystals suitable for X-Ray structure analysis where grown at the layer interface by freezing and layering both educt benzene solutions and letting them thaw slowly. $C_{58}H_{74}Lu_2O_2W_2$ (1704.66): Calcd. C 40.87, H 4.38; found C 41.25, H 4.35; ^{1}H NMR (400 MHz, [D$_6$]benzene): δ = -13.69 (s, 4H, J_{WH} = 83.3 Hz, W-*H*), -13.27 (s, 2H, J_{WH} = 104.1 Hz, W-*H*), 1.66 (s, 36H, C(C*H*$_3$)$_3$), 4.13 (s, 4H, C$_5$*H*$_4$), 4.24 (s, 10H, C$_5$*H*$_5$), 4.36 (s, 4H, C$_5$*H*$_4$), 4.53 (s, 2H, C$_5$*H*$_4$), 4.64 (s, 2H, C$_5$*H*$_4$), 5.16 (s, 2H, C$_5$*H*$_4$), 5.54, (s, 2H, C$_5$*H*$_4$), 6.85 (t, 2H, J_{HH} = 7.7 Hz, *p*-$C_{14}H_{21}O$), 7.38 (d, 4H, J_{HH} = 7.7 Hz, *m*-$C_{14}H_{21}O$) ppm.Due to the poor solubility of compound **1** meaningful ^{13}C NMR experiments were not possible.

Synthesis of $[C_{58}H_{73}Lu_2O_2ReW_2]$ (2a):

To $[Cp_2WH_2]$ (31.6 mg, 100 µmol) in benzene (1 mL) was added $[Lu(OAr)(Cp_2Re)R(thf)]$ (85.6 mg, 100 µmol) in benzene (2 mL). The reaction mixture turned from light yellow to orange within one hour. Concentration in vacuum yielded yellow block-like crystals at 10° C. Yield: 0.408 g, 48%.$C_{58}H_{73}Lu_2O_2ReW_2$ (1706.02): Calcd. C 40.83, H 4.31; found C 40.29, H 4.16; ^{1}H NMR (400 MHz, [D$_6$]benzene): δ = -13.61 (s, 4H, J_{WH} = 82.5 Hz, W-*H*), 1.53 (s, 18H, C(C*H*$_3$)$_3$), 1.65 (s, 18H, C(C*H*$_3$)$_3$), 4.20 (s, 5H, (C$_5$*H*$_5$)Re), 4.24 (s, 10H, (C$_5$*H*$_5$)W), 4.40 (s, 2H, C$_5$*H*$_4$), 4.55 (s, 2H, C$_5$*H*$_4$), 4.83 (s, 2H, C$_5$*H*$_4$), 5.21 (s, 2H, C$_5$*H*$_4$), 6.83 (t, 1H, J_{HH} = 8,0 Hz, *p*-$C_{14}H_{21}O$), 6.85 (t, 1H, J_{HH} = 8.2 Hz, *p*-$C_{14}H_{21}O$), 7.29 (d, 2H, J_{HH} = 7.7 Hz, *m*-$C_{14}H_{21}O$), 7.38 (d, 2H, J_{HH} = 7.7 Hz, *m*-$C_{14}H_{21}O$);^{13}C NMR (100 MHz, [D$_6$]benzene): δ = 32.28 (C(*C*H$_3$)$_3$), 35.48 (*C*(CH$_3$)$_3$), 64.55 ((C$_5$H$_5$)Re), 71.62 ((C$_5$H$_5$)W), 73.73 (C$_5$H$_4$), 78.10 (C$_5$H$_4$), 117.67 (*p*-$C_{14}H_{21}O$), 125.63 (*m*-$C_{14}H_{21}O$), 137.90 (*o*-$C_{14}H_{21}O$), 163.16 (*i*-$C_{14}H_{21}O$) ppm.

Synthesis of $[C_{58}H_{73}Lu_2Mo_2O_2Re]$ (2b):

To $[Lu(OAr)(Cp_2Re)R(thf)]$ (0.428 g, 500 µmol) in benzene (10 mL) was added $[Cp_2MoH_2]$ (0.114 g, 500 µmol) in benzene (5 mL). The yellow solution turned dark orange to brown within one hour. Concentration in vacuum gave yellow crystals with a block shaped habit at 10° C. Yield: 0.198 g, 52%. $C_{58}H_{73}Lu_2Mo_2O_2Re$ (1530.22): Calcd. C 45.52, H 4.81; found C 45.02, H 4.32;^{1}H NMR (400 MHz, [D$_6$]benzene): δ = -10.25 (s, 4H, Mo-*H*), 1.52 (s, 18H, C(C*H*$_3$)$_3$), 1.65 (s, 18H, C(C*H*$_3$)$_3$), 4.20 (s, 5H, (C$_5$*H*$_5$)Re), 4.24(s, 2H,C$_5$*H*$_4$), 4.36 (s, 10H, (C$_5$*H*$_5$)Mo), 4.53 (s,

2H, C_5H_4), 4.82 (s, 2H, C_5H_4), 5.16 (s, 2H, C_5H_4), 6.82 (t, 1H, J_{HH} = 7.7 Hz, *p*-$C_{14}H_{21}O$), 6.84 (t, 1H, J_{HH} = 7.7 Hz, *p*-$C_{14}H_{21}O$), 7.28 (d, 2H, J_{HH} = 7.7 Hz, *m*-$C_{14}H_{21}O$), 7.36 (d, 2H, J_{HH} = 7,7 Hz, *m*-$C_{14}H_{21}O$); ^{13}C NMR (100 MHz, [D_6]benzene): δ = 32.71 ($C(CH_3)_3$), 35.49 ($C(CH_3)_3$), 64.55 ((C_5H_5)Re), 75.59 ((C_5H_5)Mo), 78.10 (C_5H_4), 88.48 (C_5H_4), 117.68 (*p*-$C_{14}H_{21}O$), 125.54 (*m*-$C_{14}H_{21}O$), 137.90 (*o*-$C_{14}H_{21}O$), 163.50 (*i*-$C_{14}H_{21}O$) ppm.

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8 List of Publications

1) C. Döring, W. P. Kretschmer, T. Bauer, R. Kempe, *Eur. J. Inorg. Chem.* **2009**, 4255–4264.
„Scandium Aminopyridinates: Synthesis, Structure and Isoprene Polymerization"

The following publications have been published, are accepted or are to be submitted during the work on this thesis:

2) W. P. Kretschmer, T. Bauer, B. Hessen, R. Kempe, *Dalton Trans*. **2010**, *39*, 6847–6852.
„An efficient yttrium catalysed version of the "Aufbaureaktion" for the synthesis of terminal functionalised polyethylene"

3) B. Wrackmeyer, E. V. Klimkina, W. Milius, T. Bauer, R. Kempe, *Chem. Eur. J*. **2011**, *17*, 3238–3251.
„Synthesis and Reactivity of 4,5-[1,2-Dicarba-closo-dodecaborano(12)]-1,3-diselenacyclopentane: Opening of the Icosahedron to Give a Zwitterionic Intermediate and Conversion into 7,8-Dicarba-nido-undecaborate(1−)"

4) B. Wrackmeyer, E. Molla, P. Thoma, E. V. Klimkina, O. L. Tok, T. Bauer, R. Kempe, *Z. Anorg. Allg. Chem.* **2011**, *637*, 401–405.
„N-Methyl-anilinoborane: Monomer, Dimers, Molecular Structure, and Rearrangement into μ-(N-Methyl-anilino)diborane(6). A Convenient Route to μ-(Amino)diboranes(6)"

5) A. Noor, E. S. Tamne, S. Qayyum, T. Bauer, R. Kempe, *Chem. Eur. J*. **2011**, *17*, 6900–6903.
"Cycloaddition Reactions of a Chromium–Chromium Quintuple Bond"

A. Noor, E. S. Tamne, S. Qayyum, T. Bauer, R. Kempe, *Chem. Eur. J*. **2011**, *17*, 6873.
„Front Cover: Cycloaddition Reactions of a Chromium–Chromium Quintuple Bond"

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8) A. P. Sobaczynski, T. Bauer, R. Kempe, *Organometallics* **2013**, *32*, 1363–1369.
„Heterometallic Hydride Complexes of Rare-Earth Metals and Ruthenium through C–H Bond Activation”

9) M. Harras, T. Bauer, R. Kempe, R. Schobert, *Tetrahedron* **2013**, *69*, 3677–3682.
„Selective O-methylations of 3-[(triphenylphosphoranylidene)acetyl]tetronic and -tetramic acids”
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10) T. Bauer, F. R. Wagner, R. Kempe, *Chem. Eur. J.* **2013**, *19*, 8732–8735.
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11) A. Noor, T. Bauer, T. K. Todorova, B. Weber, L. Gagliardi, R. Kempe, *Chem. Eur. J.* **2013**, *19*, 9825–9832.
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13) T. Bauer, R. Kempe, to be submitted.
„Synthesis and Structure of a Trinuclear Yttrium Polyhydride Cluster Stabilized by a Bulky Guanidinate Ligand”

14) T. Bauer, W. P. Kretschmer, M. Hafeez, R. Kempe, to be submitted.
„Synthesis and Structure of Aminopyridinato and Guanidinato Ligand Stabilized Al-H Complexes”

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10 Declaration / Erklärung:

I hereby declare that I have written this work by myself and that no other sources than those mentioned in this work have been used.

This work has so far neither been submitted to the Faculty of Biology, Chemistry and Earth Sciences at the University of Bayreuth nor to any other scientific institution for the purpose of a doctoral thesis. I never finally failed a similar doctoral examination at any other university.

Hiermit versichere ich an Eides statt, dass ich die vorliegende Arbeit selbstständig und nur unter Verwendung der angegebenen Hilfsmittel und Quellen angefertigt habe.

Diese Arbeit wurde bisher weder an der Fakultät für Biologie, Chemie und Geowissenschaften der Universität Bayreuth noch einer anderen wissenschaftlichen Einrichtung zum Zwecke der Promotion eingereicht. Ich habe keine gleichartige Doktorprüfung an einer anderen universitären Hochschule endgültig nicht bestanden.

Tobias Bauer