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Review

# Towards f and d electron interactions in amido metal complexes

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## Abstract

A short review of heterobimetallic amido complexes incorporating lanthanides and Group 9 or 10 metals is given. The use of bisaminopyridinato ligands allows the isolation of compounds with very short metal–metal distances. The reaction of bisaminopyridinato ‘ate’-complexes with late transition metal chlorides gives rise to such complexes if the ligand transfer from the lanthanide center to the late transition metal can be avoided.

*Keywords:* Amido; Heterobimetallic; Aminopyridinato

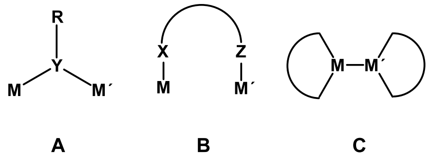
## 1. General remarks

### 1.1. Bimetallics

A continuing challenge in the coordination chemistry is the preparation of heterobimetallic complexes, and in particular the synthesis of systems, that contain both an early (electron-deficient) and a late (electron-rich) transition metal. Interesting characteristics like multi-functionality and cooperative effects of totally different transition metals can be expected [1,2]. The cooperation of two metals can result in interesting properties in areas of material science [3–5] and homogeneous catalysis [6]. Furthermore, a well-defined single metal center can benefit from a second metal in terms of reactivity. The incorporation of a ‘hard’ [7] metal center into a ‘soft’ [7] mononuclear transition metal complex can cause changes in reactivity and selectivity. For example, this has been shown for Ti–Rh and Zr–Rh complexes in hydroformylation reactions [8]. The synthesis of early–late heterobimetallics (ELHB) is complicated due to the quite different coordination demands of the two metals, especially if close proximity is desired. Three general types of ELHB are known. Firstly, the metals can be connected via a single coordination site (**A**). Amides, phosphides, halogenids, carbonyls, alkyls, or hydrides can act as such a bridge. Secondly, ligands that contain a ‘hard’ and a ‘soft’ donor center can be introduced (**B**). Thirdly, a direct metal–metal bond can be established (**C**). Types **A** and **B** are the most common (Scheme 1).

### 1.2. f and d Electron interactions

Considering possible combinations of early and late transition metals, Group 3 (G3) metals or lanthanides and Groups 8–10 metals seem to have the most different coordination chemistry behavior and, thus, have to be considered as the most challenging one to establish metal–metal communication. Many well-defined bi and multi-metallic complexes of these metals are known: G3–Fe [9], Ln–Fe [9a,10], Ln–Ru [11], G3–Co [12], Ln–Co [10b,13], Ln–Rh [14], Ln–Ir [15], G3–Ni [16], Ln–Ni [16a–e,i,17], Ln–Pd [14,17f,18], Ln–Pt [17m,19]. The discussion of some of these compounds is limited to examples, which are considered as milestones



Scheme 1. Simplified binding modes in heterobimetallics: (M = ‘early’, ‘hard’, M′ = ‘late’, ‘soft’ transition metal) **A** = single-site bridged, **B** = multi-dentate ligand bridged (X = ‘hard center’, Z = ‘soft center’), **C** = unsupported metal–metal bonds.

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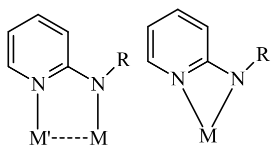
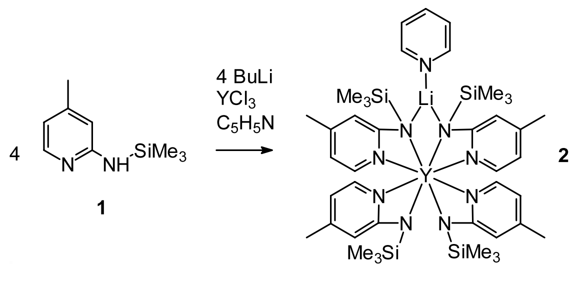
in coordination chemistry. The reaction of tris(cyclopentadienyl) lanthanide complexes with transition metal carbonyls gave rise to heterobimetallics combining a Ln center and a Groups 8–10 metal [20,21]. These compounds were not characterized via X-ray single-crystal structure analysis (X-ray analysis). A Ln–O–C–M′ binding pattern was concluded from spectroscopic data. The reduction of [$Co_2(CO)_8$] and [$Fe_3(CO)_{12}$] with the divalent lanthanide complex [$Cp^*_2Yb(OEt_2)$] (Cp* = Pentamethylcyclopentadienyl ligand, Et = ethyl) leads to [$Cp^*_2$(thf)Yb(μ-OC)$Co(CO)_3$] [13b] and [$Cp^*_2Yb$]$_2$[(μ-OC)$_4Fe_3(CO)_7$] [10a]. Both compounds were investigated via X-ray analysis. The cationic, trivalent Yb complex moiety is connected to the late metal anion via an elongated CO bridge, and a conjugated charge density distribution $M'(\delta-)$–$C(\delta+)$–$O(\delta-)$–$Yb(\delta+)$ (M′ = Co, Fe) was observed. Thus, the reactivity of the bridging carbonyl could be considered as enhanced due to this activation. In the course of reactivity studies of divalent Ln-centers towards transition metal carbonyls the synthesis of [$SmI_2(thf)_5$][$Co(CO)_4$] was reported (thf = tetrahydrofuran) [13e]. In contrast to the compounds mentioned above there was no bridging carbonyl but instead, a salt-like structure with a separated cation and anion was found. Oxygen donor atoms of the acac ligands which act as bridges between the two metal centers could be observed in [$Eu(fod)_3Co(acac)_3$] synthesized from the lanthanide shift reagent [$Eu(fod)_3$] (fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octandionate; acac = acetylacetonate) [13a]. In 1987 the synthesis and structure of [$Cp^*_2Yb$(μ-$C_2H_4$)$Pt(PPh_3)_2$] (Ph = Phenyl) [19a], the first stable and isolated π-coordinated olefin lanthanide complex [22], was reported. The reaction of [$Yb(thf)_2(C_5H_4PPh_2)_2$] with [(cod)$PtMe_2$] (cod = 1,5-cyclooctadiene; Me = methyl) gave rise to [$(thf)_2Yb(C_5H_4PPh_2)_2PtMe_2$, a complex for which a metal–metal separation of 5.01 Å was described [19b]. A significantly shorter distance between the metals (4.04 Å) was observed for [$Cp^*_2Yb$(μ-$CH_3$)$_2$Pt(dippe)] [19c] (dippe = 1,2-bis(diisopropylphosphino)ethane). Formal exchange of the bridging methyl groups by hydride ligands leads to a further decrease of the metal separation, 3.39 Å in [$Cp^*_2Yb$(μ-$CH_3$)(μ-H)Pt(dippe)] and 3.26 Å for [$Cp^*_2Yb$(μ-H)$_2$Pt(dcype)] (dcype = 1,2-bis(dicyclohexylphosphino)ethane). Samarium and iron were combined in [$Cp^*_2Sm$(μ-OC)$_2$FeCp*]$_2$ [10i], which μ-CO bridges connect the metal centers in. The introduction of phosphacyclopentadienyl ligands allows the stabilization of bimetallics such as [$(thf)_2Yb(C_4Me_4P)_2$]-[$RuH_2(PPh_3)_2$] [11a] or [(carbene)$Yb(C_4Me_4P)_2$]-[$RuH_2(PPh_3)_2$] [11e] where the Cp moieties coordinate the Yb and the phosphorus functions coordinate Group 8 metal (carbene = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene). A short metal–metal distance (Ni–Eu 3.26 Å) was observed in [$(dmf)_8Ln_2Ni(NCO)_8$] (Ln = Sm, Eu, dmf = dimethylformamide) by using isocyanate ligands [17c]. The metals are connected via three of these ligands. The only example of a combination of a Group 3 metal or a lanthanide with iridium is [$Cp^*_2Cl_2Sm$][Cp*2Ir] [15], an anion–cation separated coordination compound. Among those distal complexes, the most exciting one probably is the $Sc_3N$ moiety contained inside a fullerene with an octa(ethyl)porphyrinato–cobalt counterpart [12b]. Examples of bimetallics containing a metal–metal bond in a more or less classical sense (like a σ-bond-type **C**) are rare. An example of such a compound is [(thf)$Cp_2Lu$–$RuCp(CO)_2$] [11b–d] with a Lu–Ru bond length of 2.96 Å. It can be concluded that the shortest distances between lanthanides and Groups 8–10 metals are around 3 Å. In terms of unsupported metal–metal bonds (type **C**), the following coordination polymers have to be discussed as well: [$(CH_3CN)YbFe(CO)_4(CH_3CN)$]$_\infty$ and [$(CH_3CN)YbFe(CO)_4$]$_\infty$ seem to have such a bond, with distances between 3.012 and 3.046 Å. Since they are coordination polymers, the molecular unit itself acts as a bridging ligand.

### *1.3. Perspectives, problems encountered and scope of the mini-review*

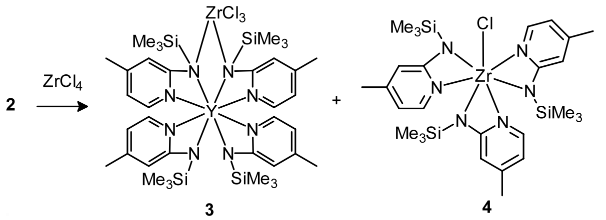
The immense interest in combining f and late d metals, especially carbonyl-containing compounds, might have been motivated by the development of homogenous analogues of the heterogeneous Fischer–Tropsch catalysts [23]. A breakthrough has not been observed so far. Many compromises have to be made to synthesize the bimetallics, and the introduction of known patterns of intrinsically active catalysts has not been considered enough. Besides catalysis, other applications are in discussion. [$Ln(hfa)_3$Ni(salen)] (Ln = Y, Gd), [16i], for example, sublimes under vacuum and, thus, might be interesting with regard to metal–organic chemical vapor deposition [3]. Furthermore, the combination of unpaired f and d electrons is a promising candidate in terms of the development of materials which act as molecular magnets [4,5]. Lanthanide copper complexes have been investigated with regard of their magneto-chemical behavior [4,24,25]. Strong interactions of d and f metals which may lead to interesting magnetic behavior that could be expected in compounds with very short distances between the two centers due to the possibility of a better overlapping of the magnetic orbitals. Amido metal complexes [26] have been investigated rarely with regard to any f, d metal combinations [14]. The fact that very short metal–metal distances are observed makes amido and, especially aminopyridinato (aminopyridinato = Ap) ligands, interesting. Today, amido metal chemistry has come to mean the utilization of the presumed disadvantage of a



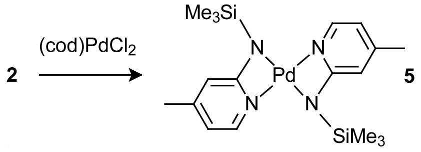
Scheme 2. Aminopyridinato ligands and their binding modes (M, M′ metals, R, for instance, alkyl, aryl, or trialkylsilyl substituents).



Scheme 3. Synthesis of **2**.



Scheme 4. Ligand transfer reactions via heterobimetallic intermediates.



Scheme 5. Synthesis of **5** via ligand transfer.

stable amido metal bond to produce well-defined reaction centers in transition metal complexes. In this way, the reactivity of the resulting compounds can be tailored specifically to allow applications in areas such as the activation of small, poorly reactive molecules, homogenous catalysis, organic synthesis, or material science. Insights into the mechanisms of elementary reactions, such as C–H activation, α-H elimination, the cleavage of the N–N triple bond, reactions of $N_2$ with $H_2$ within the coordination sphere of transition metals, new routes for the synthesis of macrocycles, polar metal–metal bonds, and complexes with unusual terminal ligands, such as phosphorus, arsenic, or carbon are, in addition to interesting transfer or polymerization reactions, just a few selected examples which illustrate, what has become possible by the use of amido ligands [27]. Aminopyridinato ligands are special amido ligands and are derived from deprotonated 2-aminopyridines (Scheme 2).

They are interesting due to the flexibility of their binding mode. Aminopyridinato ligands can coordinate in a strained $\eta^2$-fashion or can act as a bridging unit (Scheme 2). The aim of this mini-review is to discuss the lanthanide coordination chemistry of aminopyridinato ligands which results in organometallics containing f and d metal mixtures with the shortest metal–metal distances observed for supported systems (see type **A** and **B** in Scheme 1) so far.

## 2. Organolanthanide chemistry with aminopyridinato ligands

### *2.1. Simple aminopyridinato ligands and their transfer reactions*

The exploration of some aspects of lanthanide and Group 3 metal coordination chemistry of aminopyridinato ligands was started with yttrium since we expected to obtain diamagnetic compounds. The in situ reaction of two, three, and four equivalents of lithiated 4-methyl-2-(trimethylsilylamino)pyridine (**1**) with dry $YCl_3$ in ether in the presence of pyridine gives the colorless yttrate complex **2** in good yields (Scheme 3) [28].

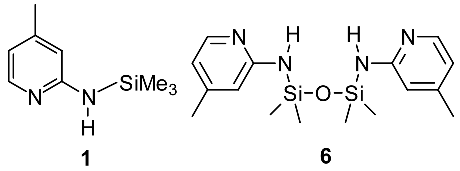
These reactions indicate that the formation of highly nitrogen coordinated ‘ate’-complexes is favored. Monochloro compounds are formed under similar conditions if cyclopentadienyl ligands [29] or silyl substituted amidinates [30,43] are used instead of **1**. Thus, a quite different Group 3 or lanthanide chemistry can be expected for aminopyridinato ligands. In the reaction of **2** with $ZrCl_4$ the complexed lithium can be replaced by a $ZrCl_3$ unit to form the extremely unstable Y–Zr heterobimetallic complex **3**, a colorless crystalline product.

Complex **3** acts as an intermediate in the transfer of ligands from yttrium to zirconium to produce **4** as a side or decomposition product (Scheme 4). An analogous ligand-transfer reaction allows access to the homoleptic amido palladium complex **5** (Scheme 5).

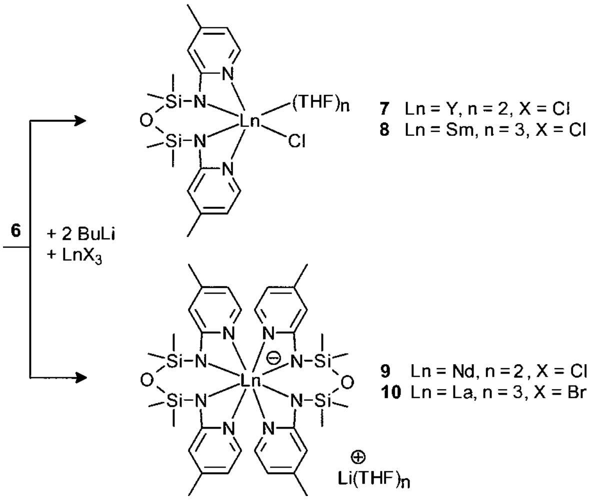
Compound **5** is an orange, crystalline complex that exhibits a $^1$H-NMR spectrum with one simple set of signals, typical of deprotonated **1**. The molecular structure of **5**, obtained by X-ray crystal structure analysis, shows two centroid coordinated aminopyridinato ligands and a planar coordination at the palladium center. The two, drastically different N–Pd–N angles, 114.55(9) and 65.45(9)°, confirm the severe strain in the complex. In the wide range of applications of palladium compounds [31], amido metal complexes have played only a secondary role to date [32]. Only a few of this class of compounds had been reported before [33]. This could be due to difficulties in the synthesis or to the instability of these compounds which arise from the 'unfortunate' combination of a 'soft' metal with the 'hard' amido ligand [7]. Besides ligand transfer, **5** can be synthesized via salt elimination reaction at low temperatures if THF is used as a solvent [28]. One of the questions arising from these studies is whether the Group 3 metal or lanthanide-mediated ligand transfer is a competitive synthetic protocol for the synthesis of amido complexes of the later transition metals especially in those cases, in which the direct synthesis failed. Bimetallics could be isolated in case of the combination Y–Zr but no stable compound with the desired Groups 8–10 metals. It was learnt that ligand transfer has to be avoided to make such ELHBs.

### *2.2. Bisaminopyridinato complexes*

One of the possibilities to avoid the ligand transfer reactions is the use of bisaminopyridinato ligands instead of ligands like deprotonated **1** (Scheme 6). Two aminopyridinato functions are not as easily transferred as one. Molecular modeling studies suggested the use of a three atoms connector between the two Ap functions to establish a stable ligand metal binding.



Scheme 6. Simple vs. bisaminopyridinato ligands.



Scheme 7. Synthesis of bisaminopyridinato complexes.

Table 1
Ring-opening polymerization of ε-caprolactone with **10** as an initiator

| $[M_0]/[I_0]$ | $M_n$ (g mol$^{-1}$) | $M_w/M_n$ |
|---|---|---|
| 100 | 25 000 | 1.7 |
| 200 | 40 000 | 1.7 |
| 300 | 51 000 | 1.7 |
| 400 | 54 000 | 1.7 |

The reaction of one equivalent of bis-lithiated **6**, generated in situ, with $LnCl_3$ (Ln = Y, Sm) in THF affords **7** and **8** via a salt metathesis reaction (Scheme 7, above) [34]. The compounds **7** and **8** were isolated from THF–ether solution after the removal of the precipitated LiCl. Colorless crystals of **7** and light orange crystals of **8** were isolated. X-ray analyses of the two compounds clearly show that the ligand array coordinates the metal in a planar fashion. The reaction of one or two equivalents of in situ generated bislithiated **6** with $NdCl_3$ or $LaBr_3$ in THF affords **9** or **10** (Scheme 7). Independent of the ratio of **6** and the lanthanide trihalogenide used, only the bis(bisaminopyridinato) complexes were isolated. NMR data of **10** indicate a highly symmetric molecule, as only one signal set is seen in the proton spectrum.

The reaction of **7** with $LiCH(SiMe_3)_2$, $(C_4H_9)_4NBH_4$ and $NaBH_4$ gave rise to corresponding bis($CH(SiMe_3)_2$) and bis($BH_4$) complexes [34]. The steric bulk of deprotonated **6** is not large enough to shield the large lanthanide ions effectively and to avoid the formation of 'ate'-complexes.

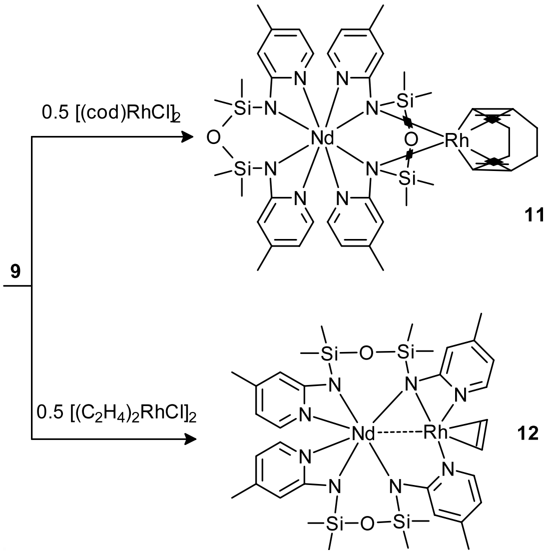
### *2.3. Ring-opening polymerizations of ε-caprolactone and δ-valerolactone using bisaminopyridinato 'ate'-complexes*

Lanthanocene complexes have been found to be initiators for the well-defined ring-opening polymerizations of ε-caprolactone and δ-valerolactone [35]. Recently, lanthanide 'ate'-complexes have been introduced as very efficient initiators [36]. However, the preferred linear relationship between the monomer to initiator ratio and the molecular weight was not observed, although molecular weights up to 30 000 g mol$^{-1}$ had been described. Thus, the aminopyridinato 'ate'-complex **10** was investigated as an initiator with regard to a linear relation between the monomer to initiator ratio and the molecular weight of the polyester, as well as in the production of high molecular weights. Tables 1 and 2 show the polymerization results.

ε-Caprolactone and δ-valerolactone were used as monomers. In both cases an almost linear relation between the monomer to initiator ratio and the molecular weight was observed. The high efficiency of the system is remarkable. By doing the polymerization in neat ε-caprolactone at room temperature a solid polyester block (300 000 g mol$^{-1}$, $M_w/M_n = 2.3$) is formed after 3 min. Nevertheless, the thermodynamically stable γ-butyrolactone could not be polymerized

Table 2
Ring-opening polymerization of δ-valerolactone with **10** as an initiator

| $[M_0]/[I_0]$ | $M_n$ (g mol$^{-1}$) | $M_w/M_n$ |
|---|---|---|
| 100 | 12 000 | 1.7 |
| 200 | 15 000 | 1.8 |
| 300 | 19 000 | 2.0 |
| 400 | 27 000 | 1.6 |



Scheme 8. Synthesis of heterobimetallic complexes.

with **10** as an initiator. Ring-opening polymerization of lactones is a useful method to produce biodegradable aliphatic polyesters [37]. Especially, well-defined polymers of this sort have interesting applications, for instance, as surgical sutures and drug delivery systems [38]. Common polyesters are made via condensation polymerization starting from diols and dicarboxylic acids. A disadvantage of this method is that high temperature and long reaction times are required to obtain high molecular weights. Furthermore, broad molecular weight distributions are observed.

## *2.4. Metal–metal communication between Nd and Rh*

Bisaminopyridinato 'ate'-complexes like **9** and **10** are analogous to **2** and expected to react with a large range of late metal chlorides. Taking the idea into account that bisaminopyridinato ligands might be able to suppress ligand transfer, compounds **9** and **10** seem to be an ideal starting material for bimetallic synthesis. The reaction of **9** with $[(cod)RhCl]_2$ in *n*-hexane gives yellow crystals of the heterobimetallic compound **11** [14].

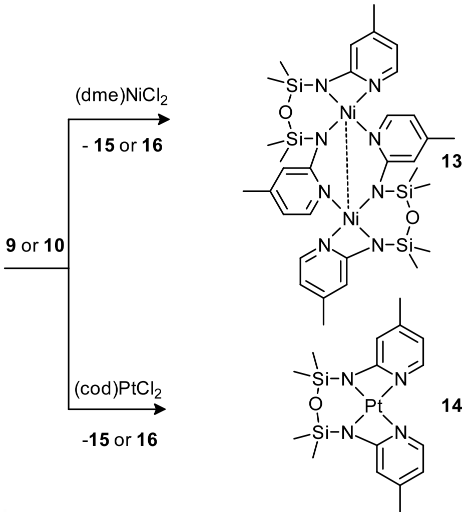
The X-ray analysis of this compound shows that there is an almost square-planar coordination at the rhodium center. A direct interaction as well as a metal–metal bond can be excluded, despite the short Nd–Rh distance of 3.2283(15) Å, since the only orbitals on the rhodium atom, which are eligible for an interaction (orthogonal to the coordination plane) [39], are not directed towards the neodymium atom. The angle between the vector parallel to the shortest metal–metal distance and the vector orthogonal to the coordination plane of the rhodium center is 50.6°. On the other hand, such an orientation of the orbitals is present in the Nd–Rh ethylene complex **12**, which is formed by the treatment of **9** with $[(C_2H_4)RhCl]_2$ (Scheme 8). The angle between those vectors in **12** is 26.9°. There is an almost planar coordination at the rhodium center of **12**. Three of the coordination sites are used by the two bis(Ap) ligands; one ligand contributes a pyridine and the other an aminopyridinato function. It is remarkable how strained amido ligands can still coordinate to late transition metal centers [N–Rh–N 64.9(2)°]. The Nd–Rh distance in **13** is 2.9744(15) Å, which is in good agreement with the value for a lanthanide late transition metal single bond [11b–d]. Metal–metal distances for unbridged single bonds have not been reported for the combinations Ln–M (M = Co, Rh or Ir). A Nd–Rh single bond, in a sense of a σ bond, cannot be assumed in **12**. It is conceivable that there is an interaction of the $d_z^2$ orbital, which is directed orthogonally to the coordination plane, with the neodymium atom comparable with a dative bond. The magnetic moments [40] of **11** ($\mu_{eff} = 4.38\ \mu_B$) and **12** ($\mu_{eff} = 4.33\ \mu_B$) correspond to the value expected for a $4f^3$ electronic configuration. For the preparation as well as the stabilization of heterobimetallic compounds like **11** and **12** is that lanthanide 'ate'-complexes like **9** and **10** react with chlorides of electron-rich transition metals by salt elimination and, that bisaminopyridinato ligands can prevent the ligand transfer from early to late transition metals and, thus, the decomposition of the bimetallic complex in case of Rh is decisive. The flexible coordination mode of the bis(Ap) ligands allows a coordinative saturation of the lanthanide metal center, leaving two or three nitrogen donor groups for a square-planar coordination at the late transition metal.

## *2.5. Bisaminopyridinato ligands and transfer reactions*

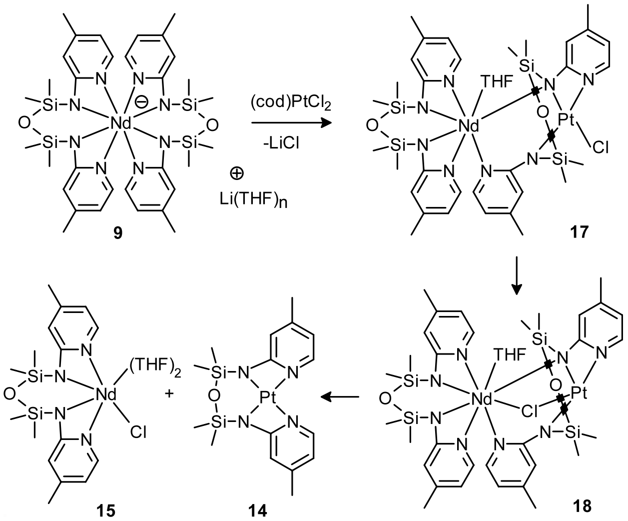
Besides Group 9 metals, the possibility of combining Nd or La with Group 10 metals was explored also. Again, ligand transfer is observed [41]. The reaction of the bis(aminopyridinato) lanthanide 'ate'-complexes **9** and **10** in hexane with $(dme)NiCl_2$ (DME = dimethoxyethane) and $(cod)PtCl_2$ leads, as shown in Scheme 9, to the dimeric Ni-complex **13** and the mononuclear platinum compound **14**, respectively. As a byproduct of both reactions, in addition to LiCl, monochloro lanthanide species $[O(SiMe_2Ap)_2LnCl(THF)_n]$ [Ln = Nd (**15**) and La (**16**); $O(SiMe_2ApH)_2 =$

6] are formed, respectively. The reaction of **1** and **2** with (cod)PdCl$_2$ only results in the formation of Pd-black, independent of the solvent used.

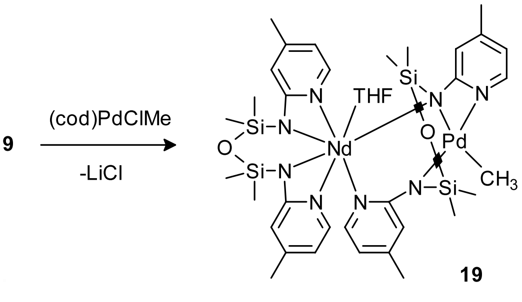
The ligand transfer reaction probably proceeds via a heterobimetallic intermediate **17** (Scheme 10). It is plausible to assume, after **17** is generated, that another heterobimetallic structure **18** with a μ-chloro bridge between the neodymium and the platinum atoms is generated. The final step in this mechanism is the transfer of the bisaminopyridanato ligand onto the platinum atom, and the transfer of the chloro functionality onto the neodymium atom. In order to support the proposed mechanism, a model of one of the intermediates (compound **19**) was synthesized.



Scheme 9. Synthesis of **13** and **14**.



Scheme 10. Proposed mechanism of the bisaminopyridinato ligand transfer reaction.



Scheme 11. Synthesis of **19**.

The heterobimetallic complex **19** was formed from the reaction of **9** with (cod)PdMeCl [42] in hexane as a light yellow powder (Scheme 11). The molecular structure of the Nd–Pd–Me complex **19** shows a planar coordination, characteristic of Pd(II) compounds. The Nd–Pd distance is 3.0345(12) Å. The two metal centers are bridged by one bis(Ap) ligand, whereas the other bis(Ap) ligand is coordinated at the neodymium. The Ap-fragment in **19** is strained in its connection to Pd as seen from a N–Pd–N angle of 64.9(3)°. The stability of **19** compared with the proposed intermediate **17** can be explained by the inhibited transfer of the methyl group. The methyl group does not have lone pairs to form the proposed chloro-bridged intermediate. Furthermore, the stability of lanthanide methyl compounds of the type [O(SiMe$_2$Ap)$_2$LnMe(thf)$_n$] has to be expected to be lower than the corresponding chloro complexes **15** and **16** [43].

Compounds **13** and **14** are late metal bisamido complexes. What about late metal amido complexes and their reactivity [44]? This chemistry still remains quite unexplored. Amido metal complexes of Group 10 [45] are known but rarely described. Compounds of such metals with bisamido ligands had been unknown to the best of our knowledge. The reactivity of late metal amido complexes, especially with regard to catalytic applications, promises to be an interesting field, because the weak amido metal bond may allow efficient generation of the catalytically active species. Thus, complex **13** was investigated with regard to catalytic applications in ethylene oligomerization after activation with aluminum alkyls. By using EtAlCl$_2$ (Al–Ni 150) in hexane at room temperature as an activator, oligoethylenes with mainly internal double bonds (Schulz–Flory distribution, TOF = 2400 h$^{-1}$) were observed. Highly branched oligomers with a very narrow molecular weight distribution [$M_n = 230$ g mol$^{-1}$ (relative to polystyrene standards), $M_w/M_n = 1.14$] are available when using Et$_3$Al$_2$Cl$_3$ as a co-catalyst and CH$_2$Cl$_2$ as the solvent (TOF = 122 000 h$^{-1}$). The ethylene consumption is nearly constant in both experiments. The products of the second oligomerization experiment, according to NMR investigations, are identical with the results published recently by Sen and co-workers [46]. A comparison of these two systems indicates that the activity of **13** is orders of magnitude higher, what may be caused by the fact that a reactive amido metal bond allows an efficient generation of the catalytically active species. The 'ate' complex mediated ligand transfer (Scheme 10) formally can be taken as a specific modification of the reactivity of lithium amides at lanthanide centers. The amides are modified in their reactivity and reductive capability via coordination at the lanthanide center. They show a reactivity high enough to react with chloro compounds of electron-rich late transition metals but these metals will not be reduced. Unstable Ln–Ni or Ln–Pt heterobimetallic complexes can be assumed as intermediates of the lanthanide-mediated ligand transfer. These intermediates most likely are important for the formation of the polycyclic and multi-nuclear structures of the resulting late metal amido complexes like **13**. The synthesis of **13** and **14** does not work—independent of the solvent and/or temperature variations, when using the dilithiated **6** and (dme)$NiCl_2$ or (cod)$PtCl_2$. A reduction of nickel is observed. The use of amines, for example, $Et_3N$, instead of BuLi as a deprotonating agent, is also ineffective.

## 3. Conclusions

Amido ligands and, especially, aminopyridinato ligands are useful to make bimetallics where in lanthanides and late transition metals are able to get in close proximity (metal–metal distances smaller than 3 Å) and an orbital arrangement can be introduced, which allows possible interactions. The nature of these communications only can be speculated, so far. Some problems and restrictions have to be discussed. Firstly, synthesis of bimetallics using deprotonated **6** is limited to larger Ln ions than Nd because no 'ate'-complexes can be synthesized for the others. Secondly, the ligand transfer has to be avoided, which could be done for selected examples of Groups 9 and 10 metals only. By the variation of the ligands or ligand systems it should be possible to address these problems [47].

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