Recent Advances in the Synthesis of N-Heteroatom Substituted Imido Complexes Containing a Nitrido Bridge [M=N-E](M = Group 4, 5 and 6 Metal, E = B, Si, Ge, P, S)

Klaus Weber, Klaus Korn, Andrea Schorm, Jennifer Kipke, Martin Lemke, Alexander Khvorost, Klaus Harms, and Jörg Sundermeyer*

Marburg, Fachbereich Chemie der Philipps-Universität Marburg, Hans-Meerwein-Straße

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Abstract. The focus of the current report lies on recent developments of synthetic methods applied to the synthesis of some high-valent complexes containing the nitrido functionality $[N]^{3-}$ as a link between a group 4, 5 or 6 transition metal and a main group element E (E = B, Si, Ge, P, S). Emphasis is put on results, that have been obtained within the "Schwerpunktprogramm "Nitridobrücken" funded by the Deutsche Forschungsgemeinschaft. The synthetic methods include condensation reactions of reactive

chloro and oxo complexes (M = V, Nb, Ta, Cr, Mo, W) with silylamines, sulfonylamides, with N-silyl and N-lithio iminophosphoranes, furthermore methatesis reactions of oxo complexes with N-sulfonyl sulfinyl amides (M = V, Cr, Mo, W), the oxidative addition of element azides to d² metal centers (M = V, W), and finally transamination reactions of N-H iminophosphoranes with amido complexes (M = Ti, Sm).

Keywords: Nitrido bridges; Imido complexes

Jüngste Fortschritte in der Synthese von N-Heteroatom-substituierten Imidokomplexen mit Nitridobrücken [M=N-E] (M = Metall der Gruppe 4, 5 und 6, E = B, Si, Ge, P, S)

Inhaltsübersicht. Der Fokus des vorliegenden Berichts liegt auf der Entwicklung synthetischer Methoden für die Synthese höhervalenter Komplexe, die eine Nitridobaugruppe $[N]^{3-}$ als Brückenfunktion zwischen einem Übergangsmetall der Gruppe 4, 5 oder 6 und einem Hauptgruppenelement E (E = B, Si, Ge, P, S) enthalten. Besonders gewichtet werden Ergebnisse, die im Rahmen des durch die Deutsche Forschungsgemeinschaft geförderten Schwerpunktprogramms "Nitridobrücken" erhalten wurden. Die synthetischen

Introduction

The chemistry of N-organoimido complexes has experienced a considerable development during the last two decades [1]. The organoimido ligand $[NR]^{2-}$ (R = alkyl, aryl) coordinates to a metal by one σ and up to two π orbital interactions, similar to the cyclopentadienyl ligand [2]. This so called cyclopentadienyl-imido-ligand-analogy [3, 4, 5] is the basis of the isolobal relationship of group 4 metallocene fragments [Ti(η^5 -C₅R₅)₂] and their corresponding imido complex fragments of group 5 and 6, [V(NR)(η^5 -C₅R₅)] and [Cr(NR)₂]. With respect to the fundamental importance of group 4 metallocenes as catalysts in olefin polymerizations and other catalytic transformations, the cyclopentadienylimido-ligand-analogy has become a strategic tool for the development of new classes of catalytically active imido

* Prof. Dr. J. Sundermeyer Fachbereich Chemie der Universität D-35032 Marburg Fax: +49-(0)6421-2828917 E-mail: jsu@chemie.uni-marburg.de Methoden umfassen Kondensationsreaktionen reaktiver Chloround Oxokomplexe (M = V, Nb, Ta, Cr, Mo, W) mit Silylaminen, Sulfonylamiden, mit N-Silyl- und N-Lithio-Iminophosphoranen, weiterhin Methatese Reaktionen von Oxokomplexen mit N-Sulfonyl-sulfinylamiden (M = V, Cr, Mo, W), die Oxidative Addition von Elementaziden an d² Metalkomplexen (M = V, W), und schließlich Transaminierungsreaktionen von N-H-funktionellen Iminophosphoranen mit Amidokomplexen (M = Ti, Sm).

complexes. Prominent examples for organoimido catalysts include vanadium [6] and chromium [7] complexes in olefin polymerizations, osmium imido complexes in the asymmetric syn-aminohydroxylation [8], molybdenum imido complexes in catalytic olefin methatesis reactions [9] and titanium imido complexes as the reactive intermediates in the amination of alkynes [10]. The donor strength and cone angle of the organoimido ligand can be controlled by the steric and electronic properties of the organic substituent within the backbone [M=N-R]. Variation of the organic radical R allows the fine-tuning of the catalyst, e.g. the first chiral, C2-symmetrical bis-imido complexes, isolobal with ansa metallocenes have been described [11]. Much less investigated are effects induced by the variation of a heteroatom subtituent E within the heteroimido donor function [M=N-E]. By considering the different bonding interactions between nitrogen and carbon compared to nitrogen and any other main group element E, it becomes clear, that heteroatom substitution will have a much greater influence on the donor properties of the ligand [M=N-E]than variations within the pattern of organic substituents R at E. The two largest classes of N-heteroatom substituted

imido complexes are those with electron withdrawing Nphosphonio $-PR_3^+$ substituents, so called phosphoraniminato complexes, and those with isoelectronically related Nsilyl $-SiR_3$ substituents. Due to the positive formal charge of the strongly electron withdrawing $-PR_3^+$ substituent, phosphoraniminato ligands are mono-anionic, while the related N-silylimido ligands are dianionic. Both ligands are less basic than organoimido ligands, therefore they may well be suitable for the design of catalytically active metal Lewis acids.

The mono-anionic ligand $[NPR_3]^-$ is bonded via one σ and up to two π bonds, it can replace a cyclopentadienyl ligand $[C_5R_5]^-$, both are considered to be isolobally related [12]. Recently, phosphoraniminato complexes of nickel [13] and titanium [14] have proven their ability to act as catalysts in olefin polymerizations and those of samarium turned out to be catalysts in the ring opening polymerization of lactones [15-18]. Nearly all of the early work with phosphoraniminato ligands focused on P-phenyl derivatives [19]. Only recently it turned out, that an even larger cone angle seems to be a precondition for the activity in olefin polymerizations: [CpTi(NPPh₃)Cl₂] and [Ti(NPPh₃)₂Cl₂] with less sterically demanding phenyl substituents were among the first d-electron poor complexes known with this ligand system [20], but they are not catalytically active in olefin polymerizations. Recently however, Stephan et al. demonstrated, that the sterically more demanding tert-butyl derivatives [CpTi(NPtBu₃)Cl₂] and [Ti(NPtBu₃)₂Cl₂] are highly active catalysts in MAO mediated a-olefin polymerizations [14]. Alkyl substituents at phosphorus also proved to generate the highly active nickel complexes in norbornene polymerization reactions [13]. Finally it has been reported, that silvlimido complexes may become active catalysts, when sterically demanding *tert*-butyl groups in [Cp* Ta(NSi^tBu₃)Cl₂] are attached at the N-heteroatom [21]. These trends demonstrate, that there is a need for developing synthetic methods for the synthesis of N-heteroimido complexes. The following report is not organized in chapters describing chemistry of a certain metal or a certain N-heteroimido ligand but in chapters describing a certain synthetic strategy of introducing a sterically demanding linkage [M=N-E] with an electron withdrawing substituent E to group 4-6 transition metals.

Results

Condensation reactions with bistrimethylsilyl amine and derivatives

Trimethylsilylimido niobium and tantalum complexes of metallocene and halfsandwich type have been obtained via condensation reactions as synthetic strategy [22]. The key complexes [M(NSiMe₃)Cl₃(py)₂] (M = Nb, Ta) are readily prepared from the metal pentachlorides and (Me₃Si)₂NH in the presence of pyridine [23]. We found that bent metallocenes $[(\eta^5-C_5H_5)_2M(NSiMe_3)Cl]$ (1a,b) and $[(\eta^5-C_5H_5)_2$ -

 $M(NSiMe_3)(\eta^1-C_5H_5)]$ (**2a,b**) are readily synthesized by reaction of $[M(NSiMe_3)Cl_3(py)_2]$ with NaCp.

Complexes with three or more σ , 2π donor ligands are π bond saturated [22]; there are more ligand orbitals of π symmetry available for π interaction than empty metal d orbitals. Therefore electron density has to remain at ligand centered non-bonding orbitals. As a consequence, both, the solid state structure of **2b** as well as dynamic nmr spectra of solutions of **2a** and **2b** reveal two η^5 - and one η^1 -cyclopentadienyl ligands. Our study proved, that a trimethylsilyl imido ligand can push a cyclopentadienyl ligand out of π coordination (Fig. 1). The σ , π bonding mode is also favored by the sterically congested situation.

In order to directly compare the σ,π -donor capability of [Me₃Si-N]²⁻ and [Me₃C-N]²⁻ ligands, two related complexes $[(\eta^5 - C_5H_5)_2 Ta(N - EMe_3)(\eta^1 - C_5H_5)] (E = Si 2b, C 2c)$ have been prepared. Both were investigated by X-ray crystallography and vt-NMR measurements. The stronger donor character of the tert-butyl imido ligand is in accord with a shorter Ta-NC bond 176.1(5) pm in 2c versus Ta-NSi 179.6(7) pm in **2b** [22]. The higher degree of $RN \rightarrow M$ π -donation and the greater sterical demand of the tertbutylimido versus silylimido ligand is responsible for a higher barrier of rotation $\Delta G^{\neq}(T_C)$ about the Ta-C_{ipso} bond of the η^1 -C₅H₅ ligand in **2c** compared to **2b**. On the other hand, the lower coalescence temperature for the σ,π -exchange of silvlimido complex 2b suggest, that the stronger donor $[NCMe_3]^{2-}$ promotes the ring slippage into a η^3 - and finally the η^1 -cyclopentadienyl bonding mode more readily than the weaker donor [NSiMe₃]²⁻. Our study is one of the very few directly comparing the bonding capability of related $[N-EMe_3]^{2-}$ ligands (E = C, Si) and adding experimental proof, that tert-butylimido ligands are the better donors than silvlimido ligands, and that both are better donors towards a d⁰ metal atom than a η^5 -C₅H₅ ligand.

Attempts to prepare halfsandwich complexes by treatment of [M(NSiMe₃)Cl₃(py)₂] with an equimolar amount of NaCp or LiCp* failed. However, the synthesis of [(η^5 -C₅Me₅)M(NSiMe₃)Cl₂] (**3a,b**) has been accomplished by reaction of [(η^5 -C₅Me₅)MCl₄] with LiN(SiMe₃)₂, while related hydridotrispyrazolylborato complexes [Tp*M-(NSiMe₃)Cl₂] (**4a, b**; Tp*= κ^3 -HB(3,5-Me₂pz)₃) have been prepared from the pyridine adducts [22]. The result of the crystal structure analysis on **4b** is shown in Figure 2. For both complex types the isoelectronic organoimido counterparts [(η^5 -C₅Me₅)M(NCMe₃)Cl₂] (M = Nb, Ta) [24] and [Tp*M(NCMe₃)Cl₂] (M = Nb, Ta) [25] are known.

Sulfonylimido complexes via arylsulfonyl sulfinylamide methatesis

Sulfonyl groups $-SO_2R$ belong to the strongest electron withdrawing substituents known. Taking the higher acidity of aryl sulfonylamides $ArSO_2NH_2$ compared to water into consideration, the donor capability of an aryl sulfonylimido ligand should be lower than that of an oxo ligand. The high reactivity of $[M=N-SO_2Ar]$ groups is reflected by the pro-



Fig. 1 Molecular structure of $[(\eta^5-C_5H_5)_2Ta(NSiMe_3)(\eta^1-C_5H_5)]$ (2b) (CCDC 132475). Selected bond distances/pm and angles/°: Ta-N 179.6(7), N-Si 170.1(8), Ta-N-Si 171.9(5).

nounced sensitivity towards hydrolysis and the tendency to undergo oxidative nitren transfer. We set out to develop a new strategy for the synthesis of electron-poor and highly reactive aryl sulfonylimido complexes containing the N-heteroatom link [M=N-S] between metals such as V, Cr, Mo and W and a six-valent sulfur atom. One of the synthetic strategies used in early work is the oxidative addition of N-Cl bonds of N,N-dichloro aryl sulfonylamides to tungsten hexacarbonyl [26, 27]. The coordination polymer **5** dissolves in MeCN to yield structurally characterized **6**.

Protolysis of $[WCl_6]$ with tosylamide offers direct access to $[W(NSO_2Tol)_2Cl_2]_n$ (7a) [28]. The by-product of aminolysis is HCl. In presence of donor ligands coordination polymer 7a can be converted into molecular complexes, e.g. $[W(NTs)_2Cl_2(dme)]$, $[W(NTs)_2Cl_2(PMe_3)_2]$ and $[W(NTs)_2-$

Fig. 2 Molecular structure of $[Tp*Ta(NSiMe_3)Cl_2]$ (4b) (CCDC 132477). Selected bond distances/pm and angles/°: Ta-N(1) 176.7(6), Si-N(1) 174.2(6), Ta-N(1)-Si 164.8(4).



 $Cl_2(4,4'-Me_2bipy)]$. For a long time, we were not able to synthesize the corresponding less stable molybdenum(VI)

C10

$$WCI_{6} + H_{2}NSO_{2}Tol \xrightarrow{-2 HCl} W(NSO_{2}Tol)_{2}CI_{2}$$

$$7a$$

$$M(O)_{2}CI_{2} + ArSO_{2}NSO \xrightarrow{-2 SO_{2}} M(NSO_{2}Ar)_{2}CI_{2}$$

$$7a \quad W, \quad Ar = 4-Tol$$

$$8a \quad Mo, \quad Ar = 4-Tol$$

$$8b \quad Mo, \quad Ar = 2,4,6-Me_{3}C_{6}H_{2}$$

$$8c \quad Mo, \quad Ar = 2,4,6-Pr_{3}C_{6}H_{2}$$

$$8a \quad 4PMe_{3} \qquad Me_{3}P \xrightarrow[-1]{N}Mo_{1}^{-PMe_{3}} + Me_{3}P=NSO_{2}Tol$$

$$9 \quad Cl$$

bis-phenylsulfonylimido complex by either oxidative N-Cl addition or protolysis strategies – "MoCl₆" is unknown, until the reaction with sulfinylamines RN=S=O was studied. Originally, we developed the sulfinylamine methatesis protocol, in order to introduce electron-withdrawing haloarylimido ligands via a desoximidation at terminal oxo complexes [29, 30]. This strategy worked well, when common strategies such as condensation reactions with silylamines failed. We learned, that methatesis of $[Mo(O)_2Cl_2]_n$ with sulfinyl sulfonylamides ArSO₂-NSO offers a straight access to highly reactive complexes of the type [Mo-(NSO₂Ar)₂Cl₂]_n (8a-c) [30].

The synthetic potential of 8a-c lies in their ability to transfer an electron-poor 6 VE nitren [NSO₂Ar] to electronrich substrates. An attempt to synthesize a molybdenum complex analogous tungsten phosphine congener $[W(NTs)_2Cl_2(PMe_3)_2]$ led to oxidative nitren transfer to the phosphine. Me₃P=NTs was formed and the d² molybdenum complex 9 was isolated and characterized by a crystal structure analysis (Fig. 3) [28]. Interestingly, a similar nitren abstraction is inhibited in the corresponding tungsten phosphine complex while the bipy complex is reacting with PMe₃ under nitren abstraction to yield [W(NTs)Cl₂- $(4,4'-Me_2bipy)(PMe_3)_2$]. This observation is in accord with a nitren transfer induced via direct attack of the phosphine HOMO into the π^* orbital of the M=NS bond (LUMO) [28].

In collaboration with the group of Hanack, another interesting reactivity pattern of $[W(NSO_2Ph)_2Cl_2]_n$ (6) has been investigated. The nitrido chlorides $[MoNCl_3]$ and $[WNCl_3]$ are good starting materials for the synthesis of novel phthalocyanine metal nitrides [PcM(N)] (10a,b) [31]. Better yields of 10b are obtained, when 6 is chosen as molecular precursor for the central [WN] building block. This may well be due to the known tendency of homolytic or heterolytic cleavage of the N-S bond within the backbone [W=N-SO₂Ph] under the reaction conditions of 220 °C. The



Fig. 3 Molecular structure of [W(NSO₂Tol)Cl₂(PMe₃)₃] (9) (CCDC 132478). Selected bond distances/pm) and angles/°: Mo-N 147.9(6), N-S 163.3(6), Mo-N-S 177.6(4).



reactivity of corresponding molybdenum tosylimido complexes is currently investigated.

We finally investigated the methatesis of $[VOCl_3]$ and $[CrO_2Cl_2]$ with arylsulfonyl sulfinylamides $ArSO_2$ -NSO. While $[VOCl_3]$ is transformed without reduction into the purple crystalline complexes $[V(NSO_2Ar)Cl_3]$ (11a,b) [30], $[CrO_2Cl_2]$ is reduced. The paramagnetic product has the composition $[\{Cr(NTs)Cl_2\}_2O]$ (13) [32] and can be envisaged as a dinuclear or oligonuclear d¹Cr-(μ -O)-Cr d¹ complex, probably formed by a combination of the Cr^{VI} species $[Cr(NTs)(O)Cl_2]$ with a coordinatively unsaturated Cr^{IV} species $[Cr(NTs)(O)Cl_2]$. The latter may have formed via an oxen abstraction from the Cr^{VI} oxo-imido intermediate by either SO₂ or TsNSO.



It is interesting to note, that $[CrO_2Cl_2]$ is not reduced by SO₂ in CCl₄/25 °C: The methatesis of $[CrO_2Cl_2]$ with slightly more electron rich C₆F₅-NSO leads selectively to SO₂ and $[Cr(NC_6F_5)_2Cl_2]$ which has been structurally characterized [30]. If the methatesis with TsNSO is performed in SO₂Cl₂ as solvent, the d¹ species $[Cr(NTs)Cl_3]$ (13) is formed. We believe, that the d² intermediate $[Cr(NTs)Cl_2]$ is quenched by chlorine radicals under these reaction conditions. Both d¹ chromium sulfonylimido complexes 12 and 13 are precursors for active Phillips-type catalysts in the MAO induced ethylene polymerisation [32, 33].

Reactions of N-silyl and N-lithio iminophosphoranes with oxo, chloro and imido complexes

Phosphoraniminato complexes are known for nearly all transition metals [19], they are the largest group of Nheteroimido compounds. As already discussed most compounds containing the nitrido bridge $[M=N=PR_3]$ have phenyl substituents at the phosphorus atom. The good availability of the reactive ligand synthon Me₃Si-N=PPh₃, its tendency to eliminate Me₃SiCl with reactive metal halides and to form highly crystalline complexes are reasons, that chemistry of iminophosphorane ligands with other P-substituents such as $R = {}^{t}Bu$, Et, Me, and NMe₂ have become popular only recently. In 1999 two reports by Stephan et al. describing the catalytic performance of sterically demanding complexes [CpTi(NP^tBu₃)Cl₂] and [Ti(NP^tBu₃)₂Cl₂] in olefin polymerisation reactions [14] pointed out the need for steric protection of the catalytically active species by bulky P-substituents. Both catalysts are isolobal with metallocene dichlorides of group 4 [Cp₂MCl₂] (M = Ti, Zr) [12, 14]. In the same year we summarized the results of our investigation of phosphoraniminato complexes of group 5 metals containing the sterically demanding P-substituents $R = NMe_2$ and ^tBu [34].

14a,b and **15a,b** are synthesized by reaction of LiNP^tBu₃ or LiNP(NMe₂)₃ with the parent metal pentachlorides. The crystal structure analysis of **15a** fills the missing link between the known structures [Nb(NPPh₃)₂Cl₃] [35] and [Ta(NPPh₃)₄]⁺[TaCl₆]⁻ [36]. The strong π donors with the high cone angle are in the equatorial positions of a trigonal bipyramid (Fig. 4). Even when an excess of LiNP^tBu₃ is reacted with **15a** for sterical reasons a tetra-substitution is not observed.

Catalysts of the type $[Cp_2TiCl_2]$, $[CpTi(NPR_3)Cl_2]$, and $[Ti(NPR_3)_2Cl_2]$ are isolobal with novel complexes of the type $[V(NR)(NPR_3)Cl_2]$. Therefore we set out to synthesize representatives of this class of imido vanadium complexes with one sterically demanding NPR₃ ligand. The synthesis



Fig. 4 Molecular structure of [Ta(NPtBu₃)₃Cl₂] (**15a**) (CCDC 117899). Selected bond distances/pm and angles/°: Ta-N1 190.6(3), Ta-N2 189.3(4), Ta-N3 190.1(4), Ta-N1-P1 170.4(2), Ta-N2-P2 171.1(2), Ta-N3-P3 168.7(2).



of **16a,b** and **17a,b** is accomplished by condensation of the precursor complexes $[V(NAr)Cl_3]$ with Me₃Si-NPR₃ (R = ^tBu, NMe₂).

The crystal structure of **16a** (Fig. 5) reveals a tetrahedral coordination at vanadium. The bonding distance of the monoanionic V-N-P ligand V-N(2) 169.5(3) pm is only slightly longer than that of the dianionic V-N-C ligand V-N(1) 167.1(3) pm. Having two sterically demanding nitrogen donors and two chloro ligands as good leaving groups these imido vanadium complexes turned out to be active catalysts in the ethylaluminium sesquichloride induced eth-ene-propene co-polymerisation leading to the synthetic elastomer EPM or terpolymer EPDM [37].

Tetrahedral molecules that contain two nitrido bridges M-N-S and M-N-P have been obtained from tungstyl and molybdyl dichloride via the sulfonyl sufinylamide methatesis followed by salt methatesis with N-lithio iminophosphoranes [38].

The molecular structure of **19a** is presented in Figure 6. The average Mo-N bonding distances for $[NSO_2Tol]^{2-}$ and $[NP^tBu_3]^-$ ligands are the same within 3 σ . In accord with this observation, both heteroimido ligands should reveal a similar donor capability.

A rather unexplored strategy for the synthesis of phosphoraniminato complexes are reactions of binary metal oxides with N-silyl iminophosphoranes [39]. We used this approach to synthesize the first chromyl $[CrO_2]^{2+}$ complexes containing the NPR₃ ligand and to develop a new most simple synthesis for chromium(VI) nitrido complexes [40].



Fig. 5 Molecular structure of $[V(N-2,4,6-Cl_3C_6H_2)(NP^tBu_3)Cl_3]$ (16a) (CCDC 198833). Selected bond distances/pm and angles/°: V-N1 167.1(3), V-N2 169.5(3), N2-P1 162.6(3), V-N1-C1 160.6(3), V-N2-P1 170.7(2).



Fig. 6 Molecular structure of[Mo(NSO₂Tol)₂(NP^tBu₃)₂] 19a (CCDC 136826). Selected bond distances/pm and angles/°: Mo-N1 181.6(2), Mo-N2 182.9(2), Mo-N3 182.0(2), Mo-N4 180.4(2), Mo-N1-P1 167.75(15), Mo-N2-P2 159.68(14), Mo-N3-S1 154.83(15), Mo-N4-S2 156.96(16).

Nitrido chromium complexes are rare [41] and there is a luck of straight forward synthetic methods for their synthesis. We discovered that polymeric CrO_3 is cut down to covalent hexane soluble chromyl silylesters 20a-c by reaction with one equivalent of the ligand precursors $Me_3Si-NPR_3$.

For sterically demanding substituents $R = {}^{t}Bu$, NMe_2 and Ph the reaction stops at this point, however for R =Me or ${}^{n}Bu$ a subsequent methatesis of the intermediate chromyl complex with a second equivalent of Me₃SiNPR₃





Fig. 7 Molecular structure of [Cr(O)₂(NPPh₃)(OSiMe₃)] **20b** (CCDC 198832). Selected bond distances/pm and angles/°: Cr-N1 173.2(4), Cr-O1 159.4(3), Cr-O2 157.7(3), Cr-O3 177.5(2), N1-P1 160.6(3), Cr-N1-P1 133.6(2).

is observed: With elimination of R_3PO chromium(VI) nitrido complexes **21a,b** are formed in perfect yield. The results of crystal structure determinations of **20b** and **21a** are shown in Figures 7 and 8.

The most striking result of these crystal structure determinations is the small angle at both Cr-N-P bond axes: 133.6(3)° (**20b**) and 127.7(4)° (**21a**). As both molecules do not show a pronounced sterically congested situation, we assume that the bending is mainly due to electronic reasons. The hard Lewis acids $[CrO_2]^{2+}$ and $[CrN]^{3+}$ seem prefer π bonding to the harder oxo and nitrido ligands rather than to the softer NPR₃ ligands. **21a** has a crystallographically imposed mirror plane defined by Cr, N1 and N2.

Oxidative addition of nitrenes generated from element azides to d^2 metal complexes

The oxidative addition of nitrenes generated from element azides R_nE-N_3 to low valent metal complexes is one of the



Fig. 8 Molecular structure of [Cr(N)(NPMe₃)(OSiMe₃)₂] **21a**(CCDC 198831). Selected bond distances/pm and angles/°: Cr-N1 173.9(6), Cr-N2 155.1(6), Cr-O1/O1a 179.3(4), N2-P1 161.7(6), Cr-N1-P1 127.7(4).



most powerful strategies to synthesize nitrido bridged compounds containing the [M-N-ER_n] link. Using this strategy *Wilkinson* et al. prepared the first borylimido complex [W(NBMes₂)₂Cl₂(PMe₃)₂] [42] whereas *Doherty* et al. were able to prepare five-coordinate bis-silylimido complex [W(NSiMe₃)₂Cl₂(PPh₂Me)] [43]. We used the azide route to synthesize five-coordinate tungsten trisimido complexes containing silyl- and borylimido ligands and to get access to a new class of N-heteroimido mesityl vanadium complexes. As highly reducing d² metal complexes for the oxidative addition of hetero-nitrenes we chose [W(NMes)₂-(PMe₃)₃] [44] and [VMes₃(THF)] [45].

Trisimido complexes tungsten complexes are very rare, they have been only characterized in a tetrahedral coordination so far [46]. Addition of the boryl azide Mes_2BN_3 to $[W(NMes)_2(PMe_3)_3]$ leads to the borylimido complex **22**. In a similar way, metal induced reduction of triorganosilyl azides leads to the silylimido complexes **23a,b**.

Both compounds 22 and 23 have been structurally characterized, the results are shown in Figures 9 and 10 [47]. Both complexes contain the three most powerful π -donor ligands in the equatorial plane of a trigonal bipyramid while the phosphine ligands occupy the axial positions.

The electron withdrawing character of the N-hetero-substituents $-SiR_3$ and $-BR_2$ is responsible for the weaker donor character and longer metal nitrogen bonds of these heteroimido ligands compared with organoimido counterparts. The boryl group in particular is a strong competitor



Fig. 9 Molecular structure of [W(NMes)₂(NBMes₂)PMe₃)₂] 22 (CCDC 198829). Selected bond distances/pm and angles/°: W-N1 184.6(6), W-N2 183.5(6), W-N3 182.8(6), N1-B 139.0(10), W-N1-B 177.7(5), W-N2-C20 171.7(5), W-N3-C10 176.4(5).



Fig. 10 Molecular structure of [W(NMes)₂(NSiMe₂'Bu)(PMe₃)₂] 23b (CCDC 198828). Selected bond distances/pm and angles/°: W-N1 180.6(4), W-N2 182.7(3), W-N3 181.7(4), W-N1-Si 169.3(2), W-N2-C20 176.9(3), W-N3-C10 171.7(4).

for the electron density at the nitrogen ligand: This is reflected by a W-N distance 4 pm longer than in silylimido counterpart **23b** and in a short B-N bond with a bond order of two, more than 4 pm shorter than in *Wilkinson'* borylimido reference complex [42].

Trimesityl vanadium [45] has been the other d² complex chosen for oxidative nitren addition reactions. The following scheme presents the scope of this synthetic strategy: V-N-B, V-N-S, V-N-Si links and the first structurally characterized example **25** of a V-N-Ge nitrido bridge have been obtained in good yields by reduction of the corresponding element azides with the vanadium(III) complex [47].

As expected, the organovanadium(V) imides are diamagnetic, orange or yellow and sensitive to light, as they are prone to homolytic V-C bond cleavage. The crystal structure of the germylimido complex **25** is shown in Figure 11. Vanadium is tetrahedrally coordinated by a linear V-N-GePh₃ group and three mesityl groups, which are twisted into a propeller-like conformation. A similar reactivity pat-





tern but limited to alkyl and silyl azides has been observed by *Gambarotta* et al. using [V(NPh₂)₃(THF)] as starting material [48].

Transamination reactions of iminophosphoranes with metal amides

The synthesis of *Stephan*-type olefin polymerization catalysts [CpTi(NP^tBu₃)Cl₂] and [Ti(NP^tBu₃)₂Cl₂] is accomplished by reaction of Me₃Si-NP^tBu₃ with the corresponding chloro complexes [14]. We were interested to develop a new synthesis for this catalyst class, as in our hands it turned out, that large scale preparations of the catalysts



are sometimes hampered by low yields due to impurities difficult to remove. Transamination reactions of metal amides with NH-functional iminophosphoranes have not been investigated in detail so far. We found that $[Ti(NMe_2)_4]$ is in close to quantitative yields transformed into *mono-* and *bis*-substituted complexes **28** and **29**.

In a similar way, $[CpTi(NMe_2)_3]$ is transformed to 31. The reaction with BCl₃ selectively replaces dimethylamino groups of these complexes by chloro ligands [49]. Our transamination strategy allows the stepwise introduction of other anionic N donors by further replacement of the amine HNMe₂: When 28 is treated with an equimolar amount of HN(C₆F₅)₂ another dimethylamido group is selectively replaced. The driving force of such transamination reactions is the demand of the electropositive metal to preferentially bind a nitrogen donor of higher group electronegativity. The molecular structure of 30 (Fig. 12) reveals three anionic nitrogen donors of different donor strength bonded to the same metal. With respect to the Ti-N bond distances the anion $[NP^{*}Bu_{3}]^{-}$ is the strongest donor, followed by $[NMe_2]^{-}$ and $[N(C_6F_5)_2]^{-}$ as the weakest donor.

Triphenylphosphoraniminato complexes of the f-block elements have been investigated by *Dehnicke* et al. [50], they reveal catalytic activity in ring-opening of lactones [15, 16, 17, 18]. The catalysts are commonly synthesized by reaction of the metal halides with Na- or KNPPh₃ [50, 51]. This strategy cannot be used for the synthesis of up to date unknown f-metal complexes with the sterically more demanding ligand $[NP^tBu_3]^-$ as it is known that its sodium or potassium salts are unstable with respect to the elimination of isobutene [52]. For this reason we extended our transamination studies towards the homoleptic bistrime-



Fig. 12 Molecular structure of $[Ti(NP^tBu_3)(NMe_2)_2\{N(C_6F_5)_2\}]$ 30 (CCDC 198834). Selected bond distances/pm and angles/°: Ti-N1 188.70(5), Ti-N2 190.61(4), Ti-N3 205.60(4), Ti-N4 178.86(4), N4-P 159.63(4), Ti-N4-P 173.06(10).



thylsilyl amides of the rare earth elements. A typical reactivity pattern is shown below for samarium, a similar is observed for yttrium.

The reaction of $[Sm{N(SiMe_3)_2}_3]$ with HNP^tBu₃ in a 1:2 molar ratio leads to **31** whereas the reaction in a 1:4 molar ratio gives an adduct **32** of HNP^tBu₃ to the Lewis acid $[Sm(NP^tBu_3)_3]$. Up to date we were not able to isolate the free Lewis acid $[Sm(NP^tBu_3)_3]$ without the neutral ligand HNP^tBu₃. The molecular structure of **32** is shown in Figure 13. The complex crystallizes in the space group I a b m with Z = 8. The molecule reveals a crystallographically imposed mirror plane defined by Sm, N1 and N3 generating N2 on symmetry equivalent positions.

The position of the hydrogen atom could not be located. We assume that it resides preferentially at N(3) having the longest of all Sm-N bonds and the smallest angle Sm(1)-N(3)-P(3) However we cannot exclude that the hydrogen atom is statistically distributed over N(1) and N(3) or over all four nitrogen atoms, as within 3 σ Sm-N(1) has the same bonding distance as Sm-N(3). Currently we are investiga-



Fig. 13 Molecular structure of [Sm(NP^tBu₃)₃(NHP^tBu₃)] 32 (CCDC 198835). Selected bond distances/pm and angles/°: Sm-N1 227.0(8), Sm-N2 223.2(8), Sm-N3 227.6(10), Sm-N1-P1 169.4(6), Sm-N2-P2 170.8(7), Sm-N3-P3 162.6(7).

ting the structure and reactivity of intermediates and progression products of this transamination cascade [49].

Outlook

The present report offers a short review on selected synthetic strategies suitable to link a transition metal M via a formal nitride N^{3-} ion to a main group element E (B, Si, Ge, P, S). Variation of the substituent E within the linkage [M-N-E] allows to control the basicity, donor strength and steric demand of these anionic nitrogen donors. The chemisty of complexes with heteroimido spectator ligands is currently investigated, as some of the complexes with 3d metals Ti, V, and Cr as well as those of rare earth metals Sm and Y turned out to be catalysts in polymerisations of olefins and oxacycles.

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