Synthesis of Nitrido(phthalocyaninato)metal(V) Complexes R_nPcMN (M = Re, Mo, W) and New Compounds with Nitrido-Bridges between Rhenium and Elements of the Third Main Group

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Abstract. New tetra- and octasubstituted nitrido(phthalocyaninato)metal(V) complexes R_nPcMN (M = Re, Mo, W) were synthesized to obtain soluble nitrido-bridged phthalocyanines. Phthalocyanines with nitrido bridges between rhenium and boron, aluminium, gallium and indium, respectively, were synthesized from nitrido(tetra-*tert.*-butylphthalocyaninato)rhenium(V) complex, tBu_4PcReN and suitable electrophilic reagents like BCl_3, $B(C_6F_5)_3$, BPh_3, BEt_3, $AlCl_3$, $GaCl_3$, $GaBr_3$, $InCl_3$, etc. The nitrido-bridged compounds prepared show different stabilities depending on the substituents at the boron atom. Additionally, the possibility to increase the nucleophilicity of $(C_5H_{11})_8PcWN$ by reducing this complex with C_8K was studied. The reaction of the reduced complex with electrophiles, e.g. with *t*BuMeSiCl, Ph_3SiCl and Me_3GeCl indicates the formation of nitrogen-bridged complexes.

Keywords: Phthalocyanines; Nitrido bridges; Nitrides; Rhenium; Tungsten; Molybdenum

Synthese von Nitrido(phthalocyaninato)metall(V)-Komplexen R_nPcMN (M = Re, Mo, W) und neuen Verbindungen mit Nitridobrücken zwischen Rhenium und Elementen der 3. Hauptgruppe

Inhaltsübersicht. Für die Darstellung von löslichen Phthalocyanin-Nitridobrücken-Verbindungen wurden neue tetra- und oktasubstituierte Nitrido(phthalocyaninato)metall(V)-Komplexe R_nPcMN (M = Re, Mo, W) synthetisiert.

Durch Umsetzung des Nitrido(tetra-*tert.*-butylphthalocyaninato)-rhenium(V)-Komplexes tBu_4PcReN mit geeigneten „elektrophilen" Reagenzien wie BCl_3, $B(C_6F_5)_3$, BPh_3, BEt_3, $AlCl_3$, $GaCl_3$, $GaBr_3$, $InCl_3$, etc. erhält man Phthalocyanin-Verbindungen mit Nitridobrücken zwischen Rhenium und Bor, Aluminium, Gallium bzw. Indium. Abhängig von den Substituenten am Bor-Atom weisen die entsprechenden Nitridobrücken-Verbindungen unterschiedliche Stabilität auf.

Zusätzlich wurde untersucht, ob sich die Nukleophilie von $(C_5H_{11})_8PcWN$ durch Reduktion mit C_8K erhöhen lässt. Die anschliessende Umsetzung des reduzierten Komplexes mit Elektrophilen z.B. mit *t*BuMeSiCl, Ph_3SiCl und Me_3GeCl deutet ebenfalls auf die Bildung stickstoffverbrückter Komplexe hin.

I Introduction

Various nitrido complexes of transition metals of groups 4 to 8 are known [1]. In 1968 *Chat* and *Heaton* reported for the first time on the synthesis of the complex, $[Re(NBX_3)Cl_2(Et_2PhP)_3]$ (X = F, Cl, Br) with a nitrido bridge between rhenium and boron [2]. Other similar complexes were synthesized by *Chat* [3], *Strähle* [4] and *Dehnicke* [5]. Reaction of $[ReNCl_2(Me_2PhP)_3]$ with BCl_3 led to $[Re(NBCl_3)Cl_2(Me_2PhP)_3]$, which was characterized by X-ray structural analysis [4]. The nitrogen atom in the complex is sp hybridized and the $M{\equiv}N{-}BCl_3$ group is linear [6]. In the meantime several groups have studied similar reactions and synthesized different nitrido-bridged compounds with Re−N−B- and Re−N−Ga-bonds [7].

The aim of our work is to prepare phthalocyanine complexes with nitrido bridges between a transition metal and a main group element. For this purpose we synthesized highly soluble peripherallysubstituted nitrido(phthalocyaninato)-metal(V) complexes. Fig. 1 shows the structures of the required tetra- (R, R' = H, *t*Bu) and octasubstituted (R = R' = CH_3, C_3H_7, C_4H_9, C_5H_{11}, C_6H_{13}, C_7H_{15}) nitrido-(phthalocyaninato)metal(V) complexes.

Nitrido(phthalocyaninato)metal(V) complexes of chromium, PcCrN [8], manganese, PcMnN [9], technetium, PcTcN [10], and rhenium, PcReN (**1**) [11,12,13], have been described. $(PcFe)_2N$ [14] and $(PcRu)_2N$ [15] are also well-known. Recently we synthesized peripherally substituted nitrido(phthalocyaninato)rhenium(V) complexes such as tBu_4PcReN (**2**) [11, 16], $(C_4H_9)_8PcReN$ (**3**), $(C_5H_{11})_8PcReN$ (**4**) [17,18], $(C_6H_{13})_8PcReN$ (**5**), $(C_7H_{15})_8PcReN$ (**6**) [17, 18] and different nitrido(phthalocyaninato)tungsten(V) com-

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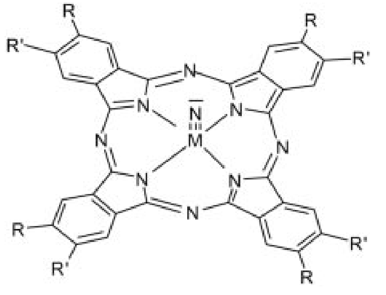


Fig. 1 Structure of Nitrido(phthalocyaninato)metal(V) Complexes

plexes, for example PcWN (**7**), tBu$_4$PcWN (**8**), $(C_5H_{11})_8$PcWN (**9**) and several nitrido(phthalocyaninato)molybdenum(V) complexes PcMoN (**10**), $(C_3H_7)_8$PcMoN (**11**), $(C_4H_9)_8$PcMoN (**12**) and $(C_5H_{11})_8$PcMoN (**13**) [19]. The terminal nitrogen ligand in nitrido(phthalocyaninato)metal(V) complexes are sufficiently nucleophilic to react with Lewis acids with formation of nitrido-bridged compounds. For example, we showed [17,20] that the reaction of BBr_3 with tBu$_4$PcReN (**2**) or $(C_5H_{11})_8$PcReN (**4**) leads to the unstable compounds tBu$_4$PcReNBBr$_3$ (**14**) and $(C_5H_{11})_8$PcReNBBr$_3$ (**15**). Thus, a nitrido bridge between rhenium and boron could be produced in this system for the first time. The reaction of acetone with the nitrido(phthalocyaninato)rhenium(V) complex is also reported [17].

We describe here the preparation of peripherally substituted rhenium, tungsten and molybdenum nitrido(phthalocyaninato)metal complexes and the reaction of tBu$_4$PcReN (**2**) and $(C_5H_{11})_8$PcWN$^-$ K$^+$ (**16**) with different electrophilic reagents.

II Results and Discussion

1 Nitrido(phthalocyaninato)metal Complexes

Scheme 1 illustrates the synthetic routes to nitrido complexes. The transition metals rhenium, tungsten and molybdenum are used as the central atom in the phthalocyanines. Soluble nitrido(phthalocyaninato)metal(V) complexes are preferred as reactants to obtain the corresponding nitrido-bridged complexes.

1.1 Nitrido(octa-n-alkylphthalocyaninato)-rhenium(V) complexes [methyl (**36**), *n-propyl* (**37**)*]*

The synthesis of $PcReSO_4 \cdot 2H_2O$ [21] from phthalonitrile and ammonium perrhenate purified with sulfuric acid, was reported in 1970 [21]. Later this compound was identified as PcReN (**1**) [12]. PcReN (**1**) can be synthesized by melting ammonium perrhenate with phthalonitrile at 280−290 °C for 50 min. Synthesis of PcReN (**1**) [13] from $ReOCl_3(PPh_3)_2$, phthalonitrile and ammonium chloride is also possible [12]. According to Scheme 1, $(CH_3)_8$PcReN (**36**) and $(C_3H_7)_8$PcReN (**37**) were prepared from 4,5-dimethylphthalonitrile (**30**) and 4,5-di-*n*-propylphthalonitrile (**31**) with ammonium perrhenate, respectively. In the IR spectrum of octasubstituted nitrido(phthalocyaninato)rhenium(V) complexes **3−6**, the Re≡N stretching frequency appears with weak intensity at $\tilde{\nu}$ = 950−1000 cm^{-1} [11−13, 16−18]. The Re≡N stretching frequency in **36** and **37** is observed at the expected region (Table 1).

Table 1 Spectroscopic Data of R_8PcReN Complexes

	IR/cm^{-1} (Re≡N)	UV/VIS/nm (Q-Band max.)
$(CH_3)_8$PcReN (**36**)	988	DMSO: 694.0
$(C_3H_7)_8$PcReN (**37**)	964	Toluene: 703.0

The corresponding Re≡N stretching frequency for OEPReN compounds lies at $\tilde{\nu}$ = 1075 cm^{-1} [22]. The lower value of the stretching vibration in PcReN can be explained by the occupation of the *trans*-position of PcReN (**1**) by the nucleophilic nitrogen atom of a neighbouring PcReN (**1**). A continuation of this principle leads to a polymeric structure, thereby the bond order between rhenium and nitrogen is reduced [11, 20].

The Q-band maxima in the UV/VIS spectra of **36** and **37** in DMSO appear in the expected region [11−13, 16−18] (Table 1) and they possess two satellite peaks. A splitting of the B bands is observed in the UV/VIS spectra of **36** and **37** and other analogous tetra- and octasubstituted nitrido(phthalocyaninato)rhenium(V) complexes [11−13, 16−18].

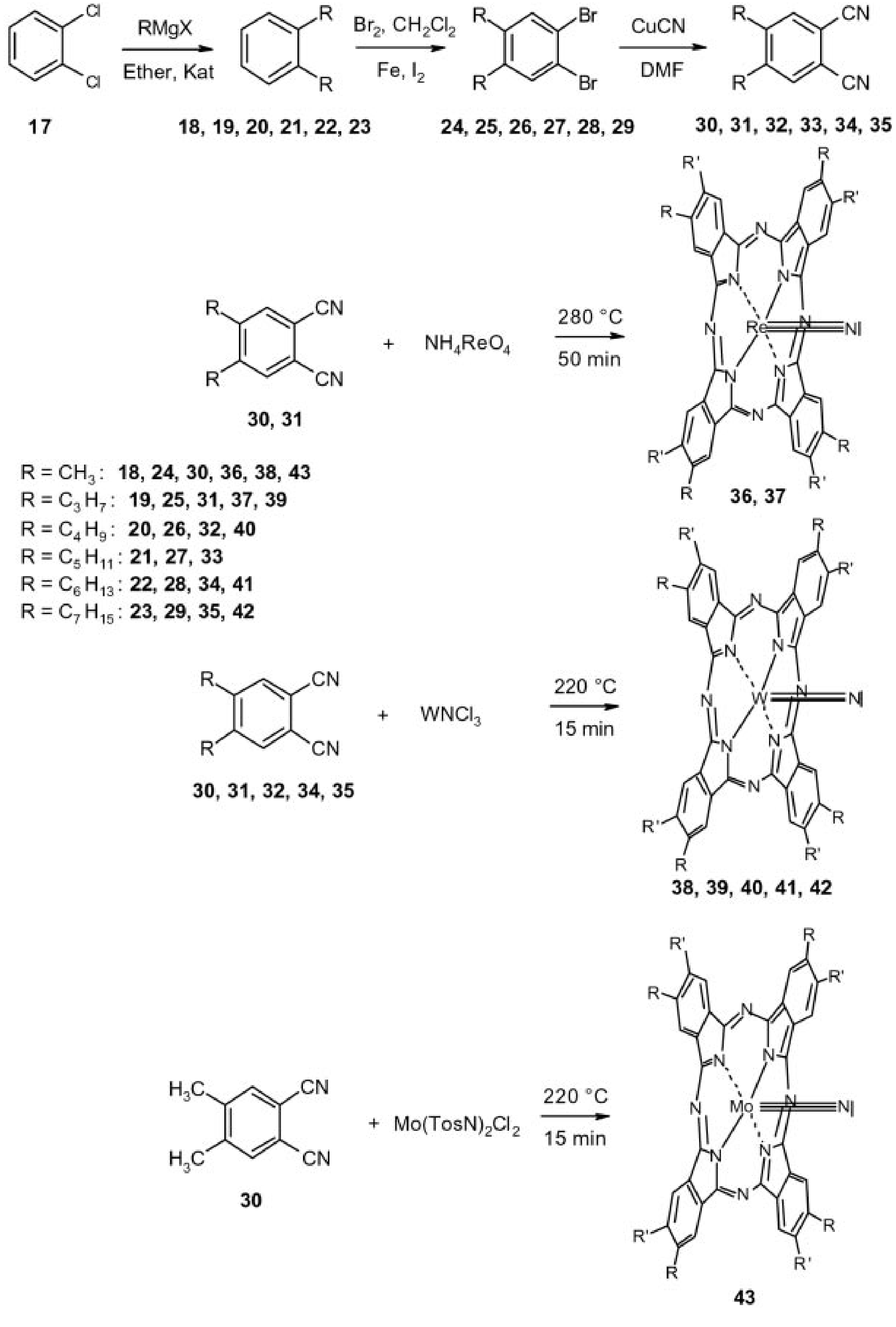
The aromatic and aliphatic protons in the ^{1}H NMR solid-state spectrum of **36** occur as singlets at δ = 7.7 (H-b) and 3.9 (H-1), respectively. In the ^{13}C CP/MAS solid-state NMR spectrum of **36**, ^{13}C signals of the aromatic carbon atoms are observed at δ = 121.6 (C-b) and the aliphatic ones at δ = 22.2 (C-1).

1.2 Nitrido(okta-n-alkylphthalocyaninato)-tungsten(V) complexes [methyl (**38**), *n-propyl* (**39**), *n-butyl* (**40**), *n-hexyl* (**41**), *n-heptyl* (**42**)*]*

Tungsten has an oxidation state of +V in $PcWCl_3$ [23] and (ClPc)W(O)OH [24]. The octasubstituted R_nPcWN complexes **38−42** are prepared in yields between 7 and 45% by melting the corresponding substituted phthalonitriles **30−32**, **34**, **35** with $WNCl_3$ [25−28] under argon (Scheme 1). The W≡N valence stretching bands in the IR spectra of PcWN (**7**), tBu$_4$PcWN (**8**) and $(C_5H_{11})_8$PcWN (**9**), are observed in the range of $\tilde{\nu}$ = 950−1000 cm^{-1} [19] and they lie also in the expected region as found for **38−41** (Table 2).

An intensive and broad signal in the ESR spectra is observed for **38** (solid state) and **39−42** (in toluene) each at g = 1.89 without hyperfine structure [19, 20].

It is possible to realize nitrido bridges in phthalocyanine complexes in one reaction step. Attempts were made to pre-



Scheme 1 Synthesis of Nitrido(phthalocyaninato)metal(V) Complexes **36**−**43**

pare $(C_5H_{11})_8PcW[N(Tos)]_2$ from $W(TosN)_2Cl_2$ [29] and 4,5-dipentyl-1,2-dicyanobenzene (**33**), however, $(C_5H_{11})_8$-PcWN (**9**) [20] was obtained. By an analogous synthetic step, the already known *t*Bu$_4$PcWN (**8**) could be synthesized. Similarly, the synthesis from $Mo(TosN)_2Cl_2$ and 4,5-dimethyl-1,2-dicyanobenzene (**30**) leads to $(CH_3)_8PcMoN$ (**43**).

1.3 Nitrido(octamethylphthalocyaninato)-molybdenum(V) (**43**)

Up to now only few phthalocyaninatomolybdenum compounds, PcMoO, PcMo(O)OH and $(PcMo)_2$ have been reported [30−35]. On the contrary, molybdenumporphyrins [36] have been better investigated, and the derivat-

Table 2 Spectroscopic Data of R_8PcWN Complexes

	IR/cm^{-1} (W≡N)	UV/VIS/nm (Q-Band max.)
$(CH_3)_8PcWN$ (**38**)	982	DMSO: 764.5
$(C_3H_7)_8PcWN$ (**39**)	957	Toluene: 759.5
$(C_4H_9)_8PcWN$ (**40**)	953	Toluene: 763.0
$(C_6H_{13})_8PcWN$ (**41**)	955	Toluene: 762.0
$(C_7H_{15})_8PcWN$ (**42**)		Toluene: 763.0

ives TMPMoN, TTPMoN and TPPMoN [37] possess some structural similarities with substituted and unsubstituted PcMoN complexes. Similar to the preparation of PcMoN [38] $(CH_3)_8PcMoN$ (**43**) can be prepared from a melt of 4,5-dimethyl-1,2-dicyanobenzene (**30**) with $Mo(TosN)_2Cl_2$ [29] at 220 °C (Scheme 1). The Mo≡N stretching frequency of several substituted nitrido(phthalocyaninato)molybdenum(V) complexes R_8PcMoN **11−13** [19] lies in the same region between $\tilde{\nu}$ = 950−1000 cm^{-1} as that of R_8PcWN and R_8PcReN [11a,16a,17,19,20]. The peak at $\tilde{\nu}$ = 991 cm^{-1} in the IR spectrum of $(CH_3)_8PcMoN$ (**43**) has been assigned to Mo≡N stretching frequency.

In the UV/VIS spectrum of $(CH_3)_8PcMoN$ (**43**) in DMF or toluene, the Q-band maximum appears at 710 nm. This value is in agreement with those found for R_8PcMoN complexes **11−13**, which is in the range of 709−716 nm [19]. The B-band of **43** in UV/VIS spectrum is found at 344 nm.

The solid-state ESR spectrum of **43** shows a broad signal with a g factor of 1.97 [19].

2 Nitrido-Bridged Compounds

The nucleophilic character of the nitrido ligand of tBu$_4$PcReN (**2**) and $(C_5H_{11})_8PcWN$ (**9**) towards various electrophiles in solution was studied. tBu$_4$PcReN (**2**) is a d^2 complex and $(C_5H_{11})_8PcWN$ (**9**) is a d^1 complex. The nucleophilicity of **9** can be increased by reducing the d^1 complex to a d^2 complex to ease the formation of a nitrido bridge by treatment of the nitrido complex with an electrophile.

2.1 Reaction of tBu$_4$PcReN (**2**) *with Electrophiles*

tBu$_4$PcReN (**2**) is soluble in organic solvents and is suitable for the synthesis of soluble phthalocyaninatometal nitrido-bridged compounds. The reaction of **2** with BEt_3, BPh_3, $B(C_6F_5)_3$, $BF_3·OEt_3$, BCl_3, $AlCl_3$, $GaCl_3$, $GaBr_3$ and $InCl_3$ leads to non-ionic, green nitrido-bridged compounds **44−53** (Scheme 2). The choice of the electrophile that has to be attached to the nitrido ligand of **2** depends on the electron-donating or -attracting ability of the substituents on the boron atom. The substituents at the boron atom influences the stability of the nitrido bridge in this system. The green ionic complex tBu$_4$PcReNSitBuMe$_2{}^+$Cl$^-$ (**54**) is also obtained by the reaction of **2** with tBuMe$_2$SiCl (Scheme 2).

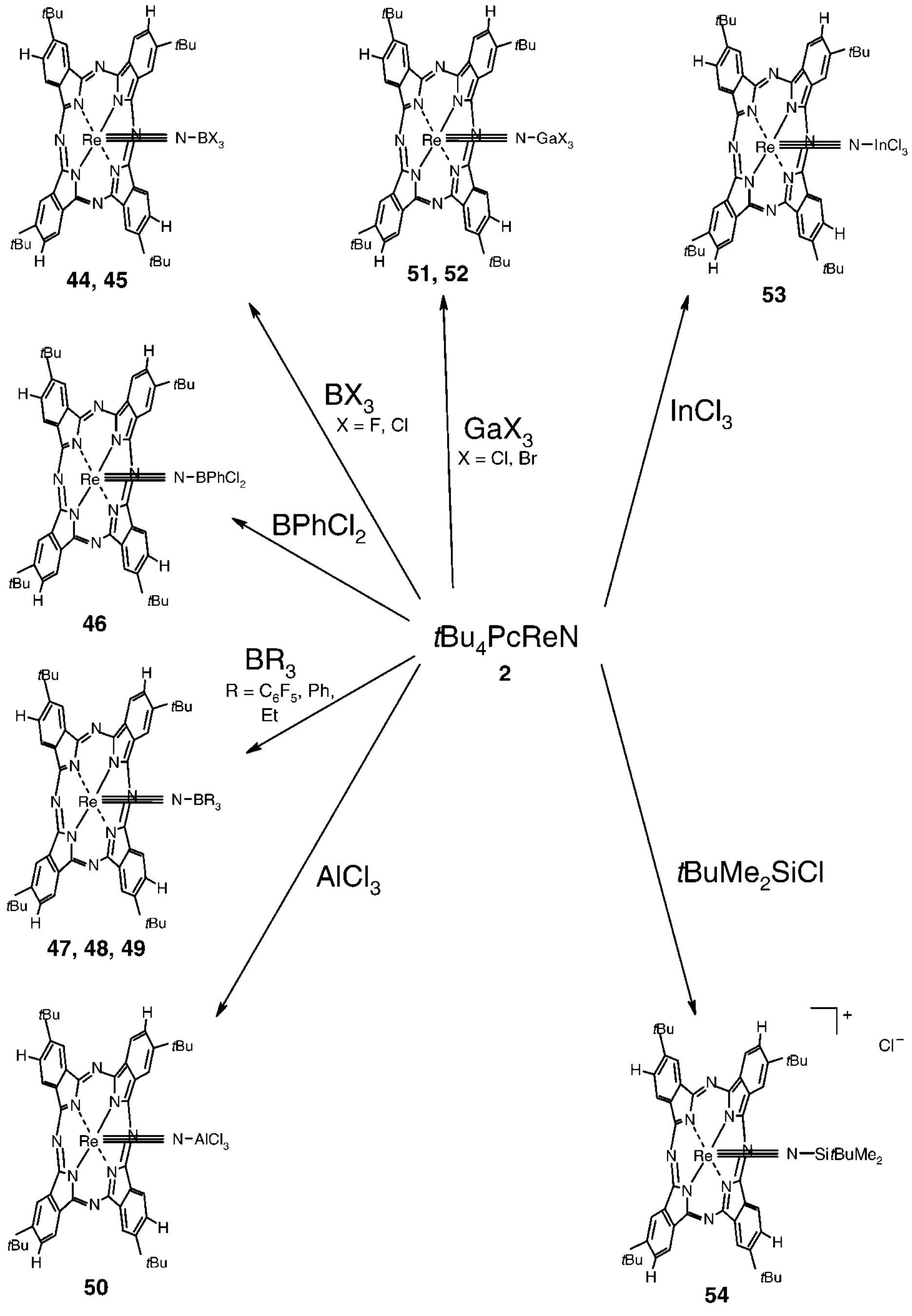
The electrophile can be removed easily from the nitrogen-bridged phthalocyninatorhenium compounds, especially in solution with the formation of tBu$_4$PcReN (**2**). The stability of the nitrido-bridged compounds **44−54** is judged with the help of UV/VIS spectra in solution.

2.1.1 Reaction of tBu$_4$PcReN (**2**) *with Boron Electrophiles*

tBu$_4$PcReN (**2**) is dissolved in dichloromethane at −5 °C to give a blue solution. On addition of appropriate electrophiles [$BF_3·OEt_2$, BCl_3, BCl_2Ph, $B(C_6F_5)_3$, BPh_3, BEt_3], the colour turns from blue to green and the solution is stirred for several hours at −5 °C till no more change of colour occurs. Reaction of $BF_3·OEt_3$ with **2** replaces the coordinated diethyl ether by the nitridophthalocyanine ligand of **2** with the formation of tBu$_4$PcReNBF$_3$ (**44**). Similarly, BCl_3 reacts with the nucleophilic nitrido ligand of $[ReN(Me_2PhP)(Et_2dtc)_2]$ to form $[Re(NBCl_3)(Me_2PhP)(Et_2dtc)_2]$ [7g]. BCl_2Ph reacts with the terminal nitrido ligands of $[ReNCl_2(Me_2PhP)_3]$, $[ReN(Cl)(MePhP)_2(Et_2dtc)]$, $[ReN(Me_2PhP)(Et_2dtc)_2]$ and $[ReNCl_2(Ph_3P)_2]$ to the corresponding "Re−N−B" complexes [7j]. Recently, compounds with nitrido bridges between Rhenium and $B(C_6F_5)_3$ [7i,k,l,m] and BPh_3 [7n] are also reported. The fragmentation pattern of nitrido-bridged compounds **44−53** in the FAB mass spectra is similar to the fragmentation pattern of *cis*, mer-$[Re(NBCl_3)Cl_2(Me_2PhP)_3]$ [4], $[Re(NBCl_3)Cl_2(Me_2PhP)_3]$ [7p] and $[Re(NBCl_3)(Me_2PhP)(Et_2dtc)_2]$ [7g] and other Re−N−B compounds [7h−r]. The structures of the prepared nitrido-bridged complexes are corroborated by elemental analyses.

An important evidence for the formation of a nitrido bridge in these systems is the shift of the Re≡N stretching vibration to higher wavelengths. $AsPh_4[ReNBr_4]$ [5], not possessing a phthalocyanine moiety, shows the Re≡N stretching vibration at 1099 cm^{-1}. The vibration is shifted to 1170 cm^{-1} for the product [5]. After reaction of boron electrophiles with the nitrido group of a rhenium complex (nitrido complex without phthalocyanine), the Re≡N stretching frequency tends to shift from 1050 to 1160 cm^{-1} [3,5,7f−q]. This shift of Re≡N stretching frequency can also be observed after the reaction of nitrido complexes $[ReNCl_2(Me_2PhP)_3]$, $[ReN(Cl)(Me_2PhP)_2(Et_2dtc)]$, $[ReN(Me_2PhP)(Et_2dtc)_2]$ and $[ReNCl_2(Ph_3P)_2]$ with boron electrophiles [7j]. The structural studies of these compounds show that the rhenium−nitrogen triple bond has only become slightly longer on account of formation of the Re−N−B bridge [7j]. The short wave length shift of Re≡N stretching frequency is explained due to the coupling of Re≡N vibration with the N−B valence vibration [7, 26].

According to this the Re≡N valence vibration band is shifted hypsochromically from $\tilde{\nu}$ = 978 to ca. 1090 cm^{-1} after the reaction of boron electrophiles with **2**. The Re≡N valence vibration band in these systems are of weak intens-



Scheme 2 Reaction of **2** with Electrophiles and $t\mathrm{BuMe_2SiCl}$

ity and is overlapped by phthalocyanine vibration signals. The Re≡N valence vibration band of **2** at $\tilde{\nu} = 978\ \mathrm{cm^{-1}}$ has disappeared in the IR spectra of nitrido-bridged compounds **44−49**. The IR spectrum of $t\mathrm{Bu_4PcReNB(C_6F_5)_3}$ (**47**) shows a characteristic band at $\tilde{\nu} = 980\ \mathrm{cm^{-1}}$, which is not due to the Re≡N valence vibration of the starting material **2**. The intensity of the peak at $\tilde{\nu} = 978\ \mathrm{cm^{-1}}$ in the IR spectrum of **2** is much weaker than that of **47**. The vibration band at $\tilde{\nu} = 980\ \mathrm{cm^{-1}}$ is also observed as highly intensive peak in other $\mathrm{M{-}N{-}B(C_6F_5)_3}$ complexes and is caused by the pentafluorophenyl groups [71].

The UV/VIS spectra of the nitrido-bridged compounds **44−49** in dichloromethane display a clear reduction of the absorption of the Q-bands after the reaction of boron electrophiles with **2**. This leads to a change in the relation of absorption of Q-bands:B-bands from 3:1 to 1:1 (Fig. 2).

When the Q-band:B-band absorption ratio does not correspond to 1:1 and changes on account of an increase of Q-band absorption, the retro-reaction to

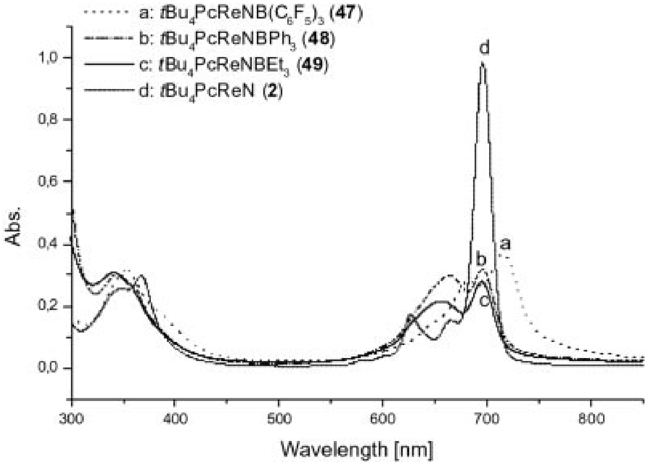


Fig. 2 UV/VIS Spectra of
a) **47** in CH_2Cl_2
b) **48** in CH_2Cl_2 between glass plates
c) **49** in CH_2Cl_2 between glass plates
d) **2** in CH_2Cl_2

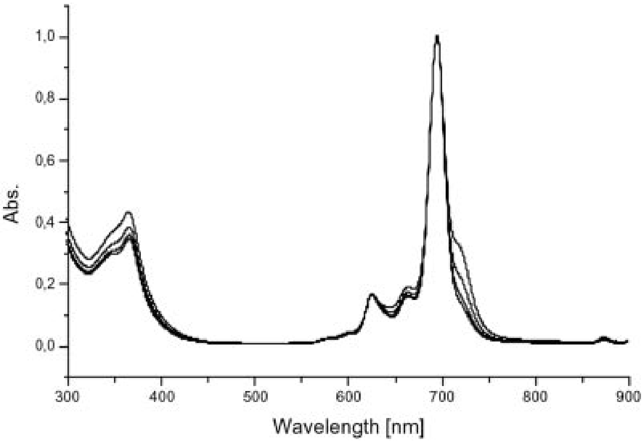


Fig. 3 UV/VIS Spectra of $t\mathrm{Bu}_4\mathrm{PcReNBCl}_3$ (**45**) in Toluene

Table 3 UV/VIS-Data of **44**−**49** in Dichloromethane

	Q-Band max./nm
$t\mathrm{Bu}_4\mathrm{PcReNBF}_3$ (**44**)	676.0
$t\mathrm{Bu}_4\mathrm{PcReNBCl}_3$ (**45**)	721.0
$t\mathrm{Bu}_4\mathrm{PcReNBCl}_2\mathrm{Ph}$ (**46**)	733.5
$t\mathrm{Bu}_4\mathrm{PcReNB(C}_6\mathrm{F}_5)_3$ (**47**)	715.5
$t\mathrm{Bu}_4\mathrm{PcReNBPh}_3$ (**48**)	695.5
$t\mathrm{Bu}_4\mathrm{PcReNBEt}_3$ (**49**)	696.0

$t\mathrm{Bu}_4\mathrm{PcReN}$ (**2**) will take place. The maximum of the Q-band of **2** in dichloromethane lies at 697 nm and contains a satellite vibration at 627.5 nm (Fig. 2d). The absorption ratio of Q-band:B-band in the UV/VIS spectrum of **2** is 3:1. Table 3 shows the UV/VIS data of **44**−**49**.

After four hours, the Q-band at 676 nm in the UV/VIS spectrum of **44** splits into two with maxima at 663 and 669 nm, which is due to the slow splitting off of boron trifluoride in **44**. After three days the Q-band maximum in the UV/VIS spectra of **44** appears at 695 nm, i.e. BF_3 has been completely split off from **44** with the formation of $t\mathrm{Bu}_4\mathrm{PcReN}$ (**2**).

The Q-band at 721 nm in the UV/VIS spectrum of $t\mathrm{Bu}_4\mathrm{PcReNBCl}_3$ (**45**) disappears completely and instead of this a Q-band of **2** at 696 nm is clearly observed. An immediate decomposition of **45** to **2** takes place by dissolving **45** in toluene instead of dichloromethane (Fig. 2d). One can notice a shoulder on the Q-band if a UV/VIS spectrum of **45** is measured during the dissolution of **45** in toluene. This shoulder is due to the decomposing product **45**. Within two minutes **45** is completely converted to $t\mathrm{Bu}_4\mathrm{PcReN}$ (**2**) and BCl_3 (cf. Fig. 3).

Even after 15 hours, the Q-band maximum can be still clearly seen in the UV/VIS spectrum of **47** in dichloromethane (Fig. 2a), which shows that **47** is more stable in the solution than **44** and **45**. Analogous to **14** (725 nm), the electron-attracting $BX_{3-n}R_n$ groups (X = Cl, Br, C_6F_5, n = 0; X = Cl, R = Ph, n = 1) are responsible for the shift of Q-bands in UV/VIS spectra of **45**−**47**. The inductive and mesomeric effects of the halogen substituent at the boron atom are probably decisive.

$t\mathrm{Bu}_4\mathrm{PcReNBPh}_3$ (**48**) and $t\mathrm{Bu}_4\mathrm{PcReNBEt}_3$ (**49**) decompose immediately in dilute solutions to the starting material (cf. Fig. 2) by changing the colour of the solution from bluish-green to blue. Concentrated solutions (dichloromethane) of **48** (Fig. 2b) and **49** (Fig. 2c) were measured between glass plates taking care that no change of colour takes place during the measurement (Fig. 2c). The UV/VIS spectrum of $t\mathrm{Bu}_4\mathrm{PcReNBPh}_3$ (**48**) is almost identical to that of $t\mathrm{Bu}_4\mathrm{PcReNBEt}_3$ (**49**) (Fig. 2c) with the Q-band maxima lying in the region of $t\mathrm{Bu}_4\mathrm{PcReN}$ (**2**). It is possible that a scission of BPh_3 or BEt_3 has already taken place during the measurement of the concentrated solution between glass plates, pointing out that the Q-band maximum of **48** and **49** is indeed that of the already formed $t\mathrm{Bu}_4\mathrm{PcReN}$ (**2**). In this connection a comparison of **47**−**49** is especially interesting, because a similar band pattern can be observed in the UV/VIS spectra (Fig. 2). The electron-attracting $B(C_6F_5)_3$ group causes only a bathochromic shift of the Q- and B-bands in the UV/VIS spectrum of **47** in comparison to $t\mathrm{Bu}_4\mathrm{PcReNBPh}_3$ (**48**) and $t\mathrm{Bu}_4\mathrm{PcReNBEt}_3$ (**49**). At the same time **47** is stabilized through the electron-attracting $B(C_6F_5)_3$ group. There is no band at 697 nm in the UV/VIS spectrum of **47** (Fig. 2a) indicating that $B(C_6F_5)_3$ is not split off from **47** and hence the starting material $t\mathrm{Bu}_4\mathrm{PcReN}$ (**2**) is not formed. The relation of Q-band:B-band is ca. 1:1 for **47**−**49** and the analogous compounds **14**, **15**, **44**−**46**. This indicates that the complex **48** and **49** have not split off BPh_3 or BEt_3 in concentrated solution (Fig. 2) and hence **2** is not formed.

^{11}B signals of four-coordinated boron atoms are already reported [39]. Fig. 4 shows the known ^{11}B NMR spectra ($CDCl_3$) of BBr_3 (Fig. 4a), **14** in test tube (Fig. 4b) and **14** after substracting the ^{11}B NMR spectrum ($CDCl_3$) of the

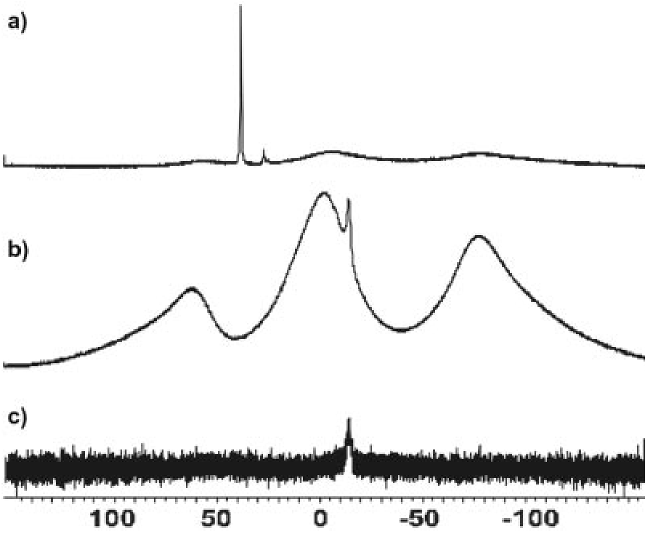


Fig. 4 ^{11}B NMR Spectrum ($CDCl_3$) of
a) BBr_3
b) $tBu_4PcReNBBr_3$ (**14**) with Test Tube
c) Difference Spectrum of **14** b) and Test Tube

test tube spectrum (Fig. 4c). The ^{11}B signal of **14** appears at $\delta = -12.90$ [17, 20].

The ^{11}B NMR spectra of **44**, **45**, **47** and **49** in CD_2Cl_2 show the ^{11}B signal in the expected region [39] using $BF_3{\cdot}OEt_2$ as standard. The boron nucleus is electron-rich due to the formation of the nitrido bridge. At the same time, the boron nucleus is influenced by the aromatic π-system of the phthalocyanine complex. The ^{11}B signals of **44**, **45**, **47** and **49** are shifted to high field in comparison to the ^{11}B signal of the boron electrophiles used. For example, the ^{11}B signals of BCl_3, BPh_3 in CD_2Cl_2 are at $\delta = 46.5$ and 68.0, respectively. The ^{11}B signal at $\delta = 45.7$ in the ^{11}B NMR spectrum of **48** is assigned to the degraded product $tBu_4PcReNBPh_2$. In comparison, ^{11}B NMR spectrum of R_2BNMe_2 (R = alkyl) give a ^{11}B NMR signal at $\delta = 45$ [40]. The ^{11}B signal of BEt_3 is located at $\delta = 86$ [41].

2.1.2 Reaction of tBu$_4$PcReN (**2**) *with AlCl$_3$, GaCl$_3$, GaBr$_3$, and InCl$_3$*

Up to now practically no information is known about nitrogen-bridged Re−Al and Re−In compounds. A solution of **2** in dichloromethane changes the colour from blue to green on addition of $AlCl_3$, $GaCl_3$, $GaBr_3$, and $InCl_3$ (Scheme 2). $[Re(NGaCl_3)(Cl)(Me_2PhP)_3(CH_3CN)]^+$ $[GaCl_4]^-$ and $[Re(NGaCl_3)Cl_2(Me_2PhP)_3]$ are known nitrogen-bridged Re−N−Ga compounds [7g,i,o,p]. The FAB mass spectrum of nitrido-bridged complexes **50**−**53** show a $[tBu_4PcReN]^+$ signal of nitrido complexes. The elemental analyses confirms the structure of **51**. $tBu_4PcReNAlCl_3$ (**50**) and $tBu_4PcReNInCl_3$ (**53**) are very labile in solution.

The Re≡N valence vibration is shifted to shorter wave length by ca. 60 cm^{-1} in the reaction of GaX_3 with the nitride of the corresponding nitrido complex [7g,i,o,p]. The Re≡N vibration band in the IR spectra of **50**−**53** are overlapped with the phthalocyanine bands and the Re≡N vibration bands of **2** at $\tilde{\nu} = 978$ cm^{-1} has disappeared.

Table 4 UV/VIS-Data for **50**−**53**

	Q-Band max./nm
$tBu_4PcReNAlCl_3$ (**50**)	696.0
$tBu_4PcReNGaCl_3$ (**51**)	720.5
$tBu_4PcReNGaBr_3$ (**52**)	721.5
$tBu_4PcReNInCl_3$ (**53**)	694.5

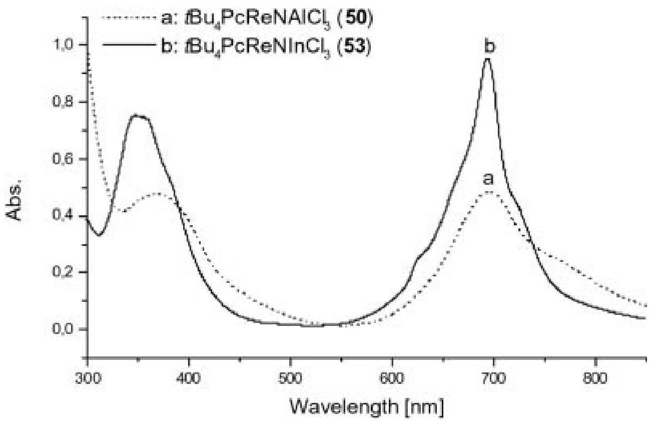


Fig. 5 UV/VIS Spectrum of
a) **50** in CH_2Cl_2
b) **53** in CH_2Cl_2

The UV/VIS data of $tBu_4PcReNAlCl_3$ (**50**), $tBu_4PcReNGaCl_3$ (**51**), $tBu_4PcReNGaBr_3$ (**52**) and $tBu_4PcReNInCl_3$ (**53**) are shown in Table 4 and confirm that the reaction of $AlCl_3$ and $InCl_3$ with tBu_4PcReN (**2**) result in $tBu_4PcReNAlCl_3$ (**50**) and $tBu_4PcReNInCl_3$ (**53**) (Scheme 2).

The decrease of Q-band absorption as compared to B-band in the UV/VIS spectrum of **50**−**53** corresponds to the already made observations, when a nitrido-bridged compound is prepared from tBu_4PcReN (**2**) and a boron electrophile. The starting material **2** is formed immediately from a dilute dichloromethane solution of $tBu_4PcReNAlCl_3$ (**50**) (cf. Fig. 2d). The recording of the UV/VIS spectra of **50** (Fig. 5a) and **53** (Fig. 5b) is possible only in concentrated dichloromethane solution between glass plates.

While recording the UV/VIS spectrum of $tBu_4PcReNGaCl_3$ (**51**) in dichloromethane, **51** is destroyed within five minutes and a Q-band maximum at 685 nm is formed.

The UV/VIS spectrum of $tBu_4PcReNGaBr_3$ (**52**) shows an already split Q-band. The same splitting of the Q-band is also observed during the decomposition of **51** indicating that **51** is more stable than **52**.

After one day, only a maximum of Q-band at 684 nm is observable in the UV/VIS spectrum of **52** (similar to the UV/VIS spectrum of **51**). While the absorption ratio of Q-band:B-band, after decomposition of **51** and **52** is ca. 1:1, a substitution of halide ion at gallium might have taken place. Thereby the nitrido bridge between rhenium and gal-

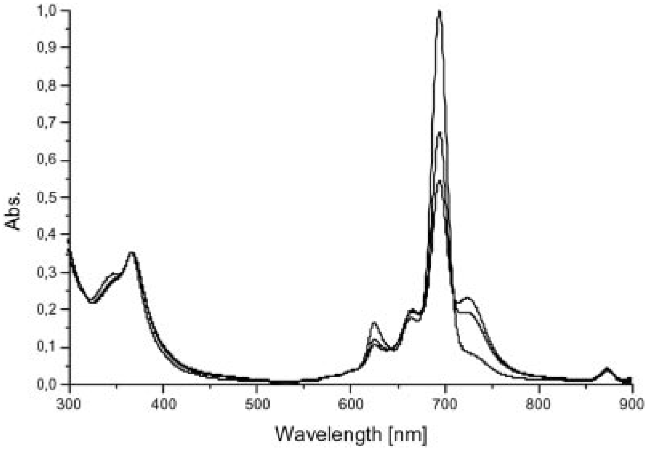


Fig. 6 Decomposition of $[^tBu_4PcReNSi^tBuMe_2]^+Cl^-$ (**54**) in Toluene

lium remains intact and the absorption relation Q-band:B-band of 1:1 is unaltered.

2.1.3. $[^tBu_4PcReNSi^tBuMe_2]^+Cl^-$ (**54**)

The ionic complex $[^tBu_4PcReNSi^tBuMe_2]^+Cl^-$ (**54**) is prepared by reacting $^tBu_4PcReN$ (**2**) with $^tBuMe_2SiCl$ (Scheme 2). The colour of the solution changes from blue to green on addition of $^tBuMe_2SiCl$ while the chloride anion of $^tBuMe_2SiCl$ is replaced by **2**. The UV/VIS spectrum of **54** shows an absorption ratio of Q-band:B-band of ca. 1:1. A weak M^+ signal of $[^tBu_4PcReNSi^tBuMe_2]^+$ and a clear peak for $[^tBu_4PcReN]^+$ can be seen in the FAB mass spectrum, showing that a substitution has taken place here. The ionic nitrogen-bridged $[^tBu_4PcReNSi^tBuMe_2]^+Cl^-$ (**54**) is a very labile compound and decomposes immediately in dilute solution (toluene) as compared to the non-ionic nitrido-bridged compounds **44**−**53**.

Analogous to the already described non-ionic nitrido-bridged compounds, the Re≡N vibration band at $\tilde{\nu}$ = 978 cm^{-1} has disappeared in the IR spectrum of **54**.

The UV/VIS spectrum of **54** is measured as a concentrated solution in toluene between glass plates and shows several Q-band maxima at 725.5, 696 and 666 nm. The maximum at 696 nm indicates a decomposition of **54** with formation of **2** (cf. Fig. 2d), which takes place within three minutes (Fig. 6).

In the UV/VIS spectrum of **54** recorded in a dilute solution of toluene, the Q-band at 695.5 nm is already larger compared to the B-band. $[^tBu_4PcReNSi^tBuMe_2]^+Cl^-$ has split off $[Si^tBuMe_2]^+$ during the dissolution process. The nitrido bridge is completely destroyed after 90 minutes and the UV/VIS spectrum of **54** corresponds to the spectrum of **2**. The maximum of the Q-band at 725.5 nm is assigned to the nitrido bridge of **54**. The UV/VIS spectrum of **45** in toluene (Fig. 3) shows similarities with the electronic spectrum of **54** (Fig. 6).

2.2 *Reduction of* $(C_5H_{11})_8PcWN$ (**9**) *and its Reaction with Electrophiles*

A d^2 complex with a high nucleophilic character is produced by reduction of a d^1 complex thereby making the reaction of electrophiles with the complex easy. Another advantage of the d^2 complex is the possibility of immediate NMR analyses of these compounds.

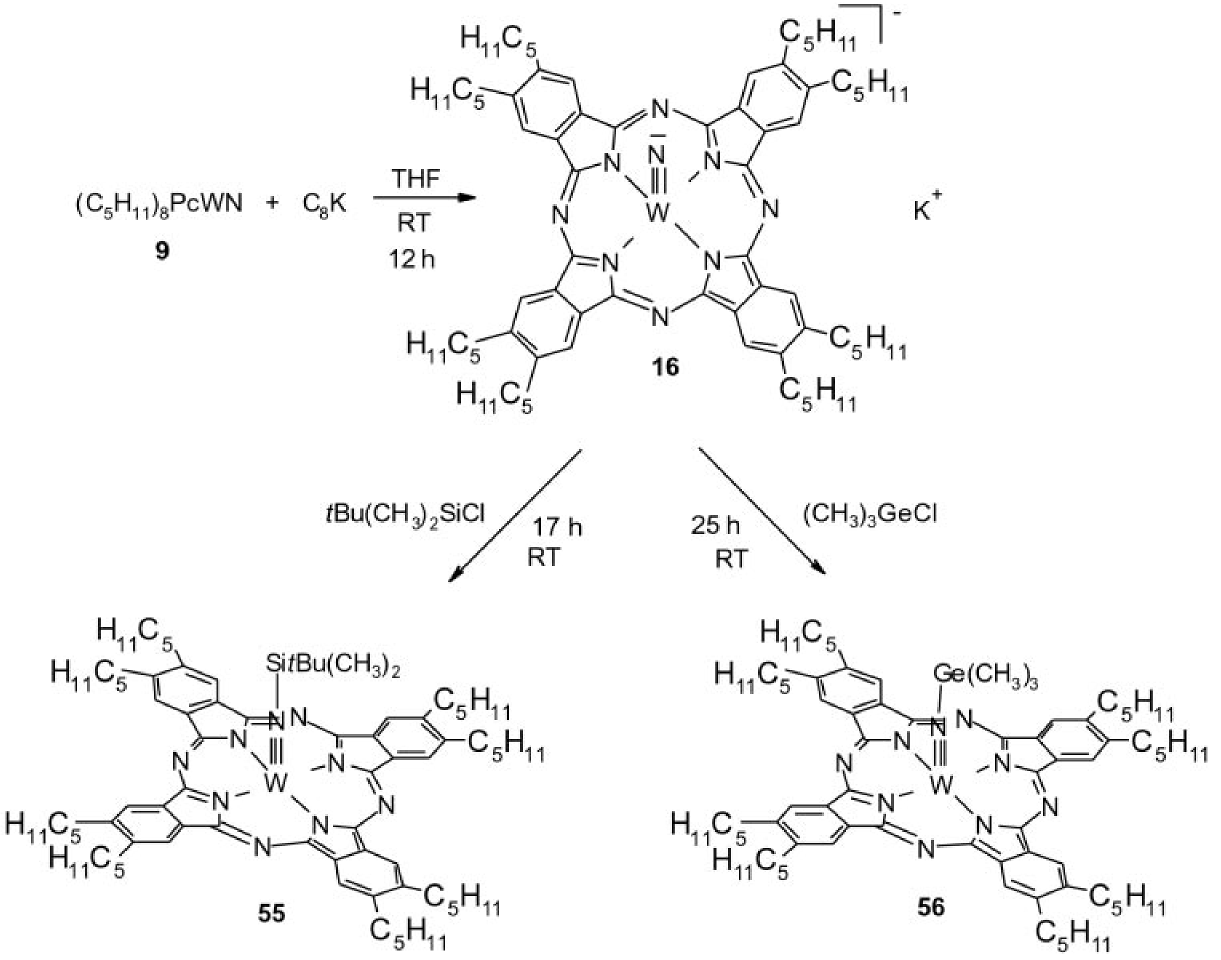
After reduction of $(C_5H_{11})_8PcWN$ (**9**) with C_8K in THF to $[(C_5H_{11})_8PcWN]^-K^+$ (**16**), the latter can form an adduct with BCl_3 to give the ionic $[(C_5H_{11})_8PcWNBCl_3]^-K^+$ or it can react with Me_3SiCl. In the latter case, the chloride ion in Me_3SiCl gets substituted by the reduced nitrido complex **16**. We have recently described this reaction [20] which gives a non-ionic compound $(C_5H_{11})_8PcWNSiMe_3$. Preliminary experiments show that **16** gives mainly a brown solution with BEt_3, $B(C_6F_5)_3$, BCl_3, BBr_3, $GaCl_3$, and $InBr_3$. Under these reaction conditions (room temperatures, 1 atmosphere) this does not lead to the expected ionic phthalocyanine complexes. Non-ionic nitrido-bridged compounds are formed in the reaction of **16** with Me_3SnCl, $tBuMe_2SiCl$, $(C_4H_9)_8PcGeCl_2$, $tBu_4PcSnCl_2$, Ph_3SiCl, Me_3GeCl, $(C_5H_{11})_8PcSi(OH)_2$, tBu_4PcSnI_2 and $tBu_4PcInCl$ by nucleophilic substitution on the „electrophiles„. The UV/VIS spectra of the compounds obtained after the reaction of **16** with $tBuMe_2SiCl$, Ph_3SiCl, Me_3GeCl, $(C_4H_9)_8PcGeCl_2$ and $tBu_4PcSnCl_2$ show Q- and B-bands which are distinctly different than the Q- and B-bands in the UV/VIS spectrum of $(C_5H_{11})_8PcWN$ (**9**). Thus, nitrido complexes are also formed here, which decompose in solution.

Scheme 3 shows the synthetic route to $(C_5H_{11})_8PcWNSi\text{-}tBuMe_2$ (**55**) and $(C_5H_{11})_8PcWNGeMe_3$ (**56**). $(C_5H_{11})_8PcWN$ (**9**) does not react with $tBuMe_2SiCl$ without reduction. The products show the M^+ signal for $[(C_5H_{11})_8PcWN]^+$ in the FD mass spectra.

The W≡N vibration of **9** at $\tilde{\nu}$ = 957 cm^{-1} is missing in the IR spectra of $(C_5H_{11})_8PcWNSitBuMe_2$ (**55**) and $(C_5H_{11})_8PcWNGeMe_3$ (**56**), but can be seen at $\tilde{\nu}$ = 1140 cm^{-1} in the IR spectra of other W−N−Si complexes [42]. Little is known on the nitrido-bridges in phthalocyanine between tungsten and silicon/germanium, and hence the assignment of W≡N in **55** and **56** is difficult.

The UV/VIS data of **55** and **56** are assembled in Table 5. The UV/VIS spectrum of $(C_5H_{11})_8PcWN$ (**9**) in toluene has a Q-band at 770.5 nm and a B-band at 376 nm. Contrary to the rhenium−nitrido bridge in phthalocyanines, the intensity of absorption of Q-band in the UV/VIS spectrum of **55** does not decrease but mainly shifts to shorter waves. An analogous blue shift is noted in the product obtained from the reduction of $(C_5H_{11})_8PcWN$ (**9**) with C_8K followed by reaction with $ClSiPh_3$ indicating that $(C_5H_{11})_8PcWNSiPh_3$ is formed.

The ^1H NMR signals for the eight pentyl groups in the periphery of **55** (in THF-d_8) appear at δ = 1.02 (H-8), 1.37 (H-7), 1.61 (H-6), 2.37 (H-5) and 2.72 (H-4). The eight aromatic protons of **55** give a multiplet at δ = 7.29−7.68. The singlets at δ = 1.29 (H-1) and 0.91 (H-2) are assigned to



Scheme 3 Reduction of **9** and Reaction with Me_3GeCl and $tBuMe_2SiCl$

Table 5 UV/VIS-Data of compounds **55** and **56**

t	Q-Band max./nm
$(C_5H_{11})_8PcWNSi^tBuMe_2$ (**55**)	725.5 (Toluene)
$(C_5H_{11})_8PcWNSi^tBuMe_2$ (**55**)	723.0 (THF)
$(C_5H_{11})_8PcWNGeMe_3$ (**56**)	731.5 (Toluene)
$(C_5H_{11})_8PcWNSiPh_3$	725.0 (THF)

the axial $SitBuMe_2$ group. The nitrogen atom in **55** between tungsten and silicon is probably sp^2 hybridized and the ^1H signal of the methyl groups at silicon is shifted downfield due to the ring current effect. This shift is also seen in the ^1H NMR spectrum of $(C_5H_{11})_8PcWNSiMe_3$ [20]. The eight pentyl substituents in the periphery of phthalocyanine **56** give five proton signals in the ^1H NMR spectrum at δ = 0.91 (H-6), 1.37 (H-5), 1.59 (H-4), 2.41 (H-3) and 2.72 (H-2). The signals for the eight aromatic protons of $(C_5H_{11})_8PcWNGeMe_3$ (**56**) appear as a multiplet at δ = 7.37−7.91. The methyl group at germanium in **56** is downfield shifted to δ = 1.3 due to the ring current of phthalocyanine, due probably to the sp^2 hybridization of the nitrogen atom between tungsten and germanium. The ^{13}C NMR spectrum of **56** (THF-d_8) shows the eight peripheral pentyl groups at δ = 13.3 (C-6), 22.4 (C-5), 30.6 (C-4), 31.7 (C-3) and 32.8 (C-2). The aromatic carbon atoms appear at δ = 123.2 (C-b), 127.1 (C-c), 129.2 (C-a) and 147.5 (C-d). The three methyl groups of **56** at germanium occur at δ = 20.4 (C-1).

III Summary

We have prepared and characterized several nitrido(phthalocyaninato)metal compounds R_8PcMN **36−43**. Our aim was to introduce a nitrido bridge between a transition metal and a main group element in phthalocyanine system.

Nitrogen-bridged compounds with different stabilities in solution are formed in the reaction of tBu_4PcReN (**2**) with different boron electrophiles. The effect of alkyl substituents instead of the halogen substituents on the boron atom on the stability of nitrido bridge between rhenium and boron in phthalocyanines has been studied.

In comparison to alkyl ligands, halogen ligands on the boron atom lead to a higher stability, i.e. the nitrogen-bridged $Re{-}N{-}BX_3$ compounds decompose slower in solution as the analogous nitrogen-bridged $Re{-}N{-}BR_3$ compounds. The stability of the nitrogen-bridged compounds increases (in solution): *t*Bu$_4$PcReNBPh$_3$ (**48**) < *t*Bu$_4$PcReNBEt$_3$ (**49**) ≤ *t*Bu$_4$PcReNBCl$_2$Ph (**46**) < *t*Bu$_4$PcReNBCl$_3$ (**45**) < *t*Bu$_4$PcReNBF$_3$ (**44**) ≈ *t*Bu$_4$PcReNB(C$_6$F$_5$)$_3$ (**47**).

The reaction of nitride **2** with GaCl$_3$, GaBr$_3$, AlCl$_3$ and InCl$_3$ leads to analogous nitrogen-bridged rhenium phthalocyanine compounds. The stability of *t*Bu$_4$PcReNGaCl$_3$ (**51**) and *t*Bu$_4$PcReNGaBr$_3$ (**52**) is comparable with **45** or **46,** and that of *t*Bu$_4$PcReNAlCl$_3$ (**50**) and *t*Bu$_4$PcReNInCl$_3$ (**53**) with **48** and **49**. The compounds are more stable in the solid state than in solution.

Treatment of *t*Bu$_4$PcReN (**2**) with *t*BuMe$_2$SiCl gives the unstable complex *t*Bu$_4$PcReNSi*t*BuMe$_2$$^+Cl^-$ (**54**).

For the preparation of nitrogen-bridged tungsten phthalocyanine compounds, the reduction of (C$_5$H$_{11}$)$_8$PcWN (**9**) with C$_8$K followed by treatment with *t*BuMe$_2$SiCl and Me$_3$GeCl, respectively, is promising. Experimental and analytical studies support that nitrido-bridged compounds are formed in each case.

IV Experimental Part

The solvents were dried according to the usual procedures [43], distilled and stored under argon. 4,5-Di-*n*-alkylphthalonitrile [alkyl = methyl (**30**), propyl (**31**), butyl (**32**), pentyl (**33**), hexyl (**34**), heptyl (**35**) [44,45], 4-*tert*-butylphthalonitrile [46], ammonium perrhenate [47], nitrido(tetra-*tert*-butylphthalocyaninato)rhenium(V) (**2**) [11,16] and nitrido(octa-*n*-pentylphthalocyaninato)tungsten (**9**) [19,20] were synthesized according to literature procedure. − EA: C, H, N: Carlo Erba Elemental Analyzer 1104 and 1106; Cl: mercurymetric titration according to Schöniger [48]. − MS: Varian MAT 711 A (FD); Finnigan ISQ 70, Varian MAT 711 A (FAB). − FT-IR: Bruker IFS 48. − UV/VIS: Shimadzu UV-2101 PC, Shimadzu UV-365. − ESR: Bruker ESP 300 (X-Band).− NMR: Bruker ARX 250 (250.1 MHz, 62.9 MHz, 80.3 MHz), Bruker ARX 400 (400.1 MHz).

1 Nitrido(phthalocyaninato)metal(V) Complexes

Nitrido(octamethylphthalocyaninato)rhenium(V) (36)

53.6 mg (0.2 mmol) NH$_4$ReO$_4$ and 156.2 mg (1 mmol) 4,5-dimethylphthalonitrile (**30**) were melted at 280 °C for 50 min. The solid residual melt was finely powdered and extracted with acetonitrile, toluene and hexane, respectively, in a Soxhlet for 5 d each. Yield: 56.0 mg (34 %), bluish-green, microcrystalline solid.

MS (FAB) (NBA, 50 °C): *m/z* = 825.1 [M$^+$]. **IR** (KBr): $\tilde{\nu}$ = 988 m cm^{-1} (Re≡N). **UV/VIS** (DMSO): λ = 363.5, 626.5, 694.0 nm. ^{1}H NMR (solid state, RT): δ = 7.7 (H-b), 3.9 (H-1). **^{13}C-CP/MAS NMR** (solid state, RT): δ = 121.60 (C-b), 22.18 (C-1).

Nitrido(octa-n-propylphthalocyaninato)rhenium(V) (37)

751.9 mg (3.542 mmol) of 4,5-dipropylphthalonitrile (**31**) and 190.0 mg (0.708 mmol) NH$_4$ReO$_4$ were melted in a Schlenk tube for 50 min at 280 °C. Die bluish-black residue was chromatographed on Al$_2$O$_3$ (neutral, 10 % H$_2$O) with toluene as eluent. After Soxhlet extraction with hexane 29 mg of (C$_3$H$_7$)$_8$PcReN (**37**) was obtained. Yield: 29.0 mg (4 %), bluish-green, microcrystalline solid.

MS (FAB) (NBA, 50 °C): *m/z* = 1049.4 [M$^+$]. **MS** (FD) (toluene, 35 °C): *m/z* = 1048.9 [M$^+$]. **IR** (KBr): $\tilde{\nu}$ = 964 m cm^{-1} (Re≡N). **UV/VIS** (toluene): λ = 351.5, 368.5, 633.0, 672.0, 703.0 nm. **^{13}C-DEPT NMR** (CD$_2$Cl$_2$): δ = 124.5 (C-b), 36.6 (C-3), 25.1 (C-2), 14.8 (C-1).

Nitrido(octamethylphthalocyaninato)tungsten(V) (38)

98.3 mg (0.63 mmol) of 4,5-dimethyl-1,2-dicyanobenzene (**30**) and 42.5 mg (0.14 mmol) of nitridotungsten trichloride were melted at 220 °C under Argon for 15 min. The residue was extracted with hexane, toluene and acetonitrile in a Soxhlet for 12 h each. Yield: 52.0 mg (45 %), dark green, amorphous solid.

MS (FAB) (NBA, 50 °C): *m/z* = 824.0 [M$^+$+H]. **IR** (KBr): $\tilde{\nu}$ = 982 vw cm^{-1} (W≡N). **UV/VIS** (DMSO): λ = 367.5, 764.5 nm. **ESR** (solid state, RT): g = 1.89.

Nitrido(octa-n-propylphthalocyaninato)tungsten(V) (39)

187.5 mg (0.88 mmol) of 4,5-dipropyl-1,2-dicyanobenzene (**31**) and 59.7 mg (0.20 mmol) of nitridotungsten trichloride were melted at 220 °C for 15 min under Argon. The crude product was extracted first with hexane in a Soxhlet and then precipitated out several times (5 ×) from toluene/hexane. Yield: 15 mg (7 %), dark green solid.

MS (FD) (toluene, 30 °C): *m/z* = 1046.4 (M$^+$). **MS** (FAB) (NBA, 50 °C): *m/z* = 1046.9 (M$^+$). **IR** (KBr): $\tilde{\nu}$ = 957 w cm^{-1} (W≡N). **UV/VIS** (toluene): λ = 374, 759.5 nm. **ESR** (toluene, RT): g = 1.89.

Nitrido(octa-n-butylphthalocyaninato)tungsten(V) (40)

151.1 mg (0.63 mmol) of 4,5-dibutyl-1,2-dicyanobenzene (**32**) and 42.5 mg (0.14 mmol) of nitridotungsten trichloride were melted at 220 °C under argon for 15 min. After Soxhlet extraction of the crude product with hexane it was precipitated out several times (5 ×) from dichloromethane/hexane. Yield: 13 mg (8 %), dark green solid.

MS (FD) (toluene, 35 °C): *m/z* = 1158.5 (M$^+$). **IR** (KBr): $\tilde{\nu}$ = 953 vw cm^{-1} (W≡N). **UV/VIS** (toluene): λ = 373.5, 763.0 nm. **ESR** (toluene, RT): g = 1.89.

Nitrido(octa-n-hexylphthalocyaninato)tungsten(V) (41)

341 mg (1.15 mmol) of 4,5-dihexyl-1,2-dicyanobenzene (**34**) and 70 mg (0.23 mmol) of nitridotungsten trichloride were melted at 220 °C for 15 min under an inert atmosphere. After a Soxhlet extraction with hexane, **41** was dissolved in hexane. The excess phthalonitrile **34** was removed at 155 °C/8·10^{-2} mbar. Yield: 68 mg (22 %), dark green solid.

MS (FD) (toluene, 35 °C): *m/z* = 1382.3 (M$^+$). **IR** (KBr): $\tilde{\nu}$ = 955 w cm^{-1} (W≡N). **UV/VIS** (toluene): λ = 374.0, 762.0 nm. **ESR** (toluene, RT): g = 1.89.

Nitrido(octa-n-heptylphthalocyaninato)tungsten(V) (42)

204.1 mg (0.63 mmol) of 4,5-diheptyl-1,2-dicyanobenzene (**35**) and 42.5 mg (0.14 mmol) of nitridotungsten trichloride were melted for 15 min at 220 °C. The crude product was washed with hexane till all the excess of phthalonitrile **35** had been removed. The hexane insoluble solid **42** was purified by extraction with hexane in a Soxhlet apparatus for 12 h. Yield: 31 mg (15 %), dark green solid.

MS (FD) (toluene, 30 °C): *m*/*z* = 1495.1 (M$^+$). **UV/VIS** (toluene): λ = 373.5, 763.0 nm. **ESR** (toluene, RT): g = 1.89.

Nitrido(octamethylphthalocyaninato)molybdenum(V) (**43**)

95.7 mg (0.61 mmol) of 4,5-dimethyl-1,2-dicyanobenzene (**30**) and 65.0 mg (0.14 mmol) ditosyliminomolybdenum dichloride were melted for 15 min at 220 °C under Argon. The residue was purified by a Soxhlet extraction with hexane, toluene and acetonitrile for 12 h each. Yield: 25.0 mg (25 %), dark green, amorphous solid.

MS (FAB) (NBA, 50 °C): *m*/*z* = 735.1 (M$^+$). **IR** (KBr): ṽ = 991 w cm^{-1} (Mo≡N). **UV/VIS** (DMF): λ = 344.0, 710.0 nm. **ESR** (solid state, RT): g = 1.97.

2 Reaction of *t*Bu$_4$PcReN (2) with Electrophiles

*t*Bu$_4$PcReN (**2**) was dissolved in ca. 5 ml dichloromethane and cooled to −5 °C. The electrophile was added dropwise to this solution. The colour of the solution changes from blue to green. The solution was stirred for 6 h at −5°C and the solvent was removed at −5 °C.

$^{t}Bu_{4}PcReNBF_{3}$ (**44**)

The reaction was conducted with 50.0 mg (0.053 mmol) of ^{t}Bu$_4$PcReN (**2**) and 9.9 mg (0.07 mmol) $BF_3{\cdot}OEt_2$. Yield: 53.6 mg (ca. 100 %), yellowish-green solid.

MS (FAB) (NBA, 50 °C): *m*/*z* = 938.2 (M$^+$−BF$_3$). **IR** (KBr): ṽ = 3422 w, 2958 m, 2866 w, 1612 s, 1483 m, 1395 m, 1365 m, 1328 vs, 1282 m, 1258 m, 1199 m, 1092 vs, 1051 vs, 964 w, 936 m, 895 w, 832 m, 766 vs, 754 vs, 693 w, 670 m, 599 vw, 564 vw, 533 w, 522 w, 441 vw cm^{-1}. **UV/VIS** (CH_2Cl_2): λ = 360.5, 676.0 nm. **^{11}B NMR** ($CDCl_3$): δ = −2.0.

$^{t}Bu_{4}PcReNBCl_{3}$ (**45**)

The reaction was conducted with 80.0 mg (0.085 mmol) of *t*Bu$_4$PcReN (**2**) and 0.085 ml (0.085 mmol) of 1 M BCl_3 solution (CH_2Cl_2). Yield: 89.8 mg (ca. 100 %), green solid. $C_{48}H_{48}BCl_3N_9Re$ (1054.4): C 51.73 (calc. 54.69); H 4.23 (4.59); N 11.38 (11.97); Cl 9.50 (9.96)%.

MS (FAB) (NBA, 50 °C): *m*/*z* = 1018.4 (M$^+$ − Cl), 937.4 (M$^+$ − BCl$_3$). **IR** (KBr, argon): ṽ = 3219 s, 2961 m, 1684 w, 1653 w, 1616 w, 1558 w, 1522 vs, 1474 vs, 1458 vs, 1437 vs, 1396 vs, 1367 vs, 1348 s, 1281 w, 1259 s, 1196 s, 1092 s, 1049 m, 1024 m, 937 vw, 833 m, 804 s, 768 w, 754 w, 667 m cm^{-1}. **IR** (KBr, air): ṽ = 3217 vs, 2963 s, 2907 m, 1518 s, 1464 vs, 1410 vs, 1369 s, 1196 s cm^{-1}. **IR** (CH_2Cl_2): ṽ = 3055 w, 2988 w, 1616 vw, 1421 vw, 1265 vs, 1200 vw, 1157 vw, 1090 w, 1018 w, 897 w, 739 vs, 706 vs cm^{-1}. **UV/VIS** (toluene): λ = 365.0, 627.0, 667.0, 696.5, 719.5 nm. UV/VIS (CH_2Cl_2): λ = 356.0, 721.0 nm. **^{11}B NMR** (CD_2Cl_2): δ = 3.4.

$^{t}Bu_{4}PcReNBCl_{2}Ph$ (**46**)

The reaction was conducted with 80.0 mg (0.085 mmol) of *t*Bu$_4$PcReN (**2**) and 13.6 mg (0.085 mmol) BCl_2Ph. Yield: 93.2 mg (ca. 100 %), green solid. $C_{54}H_{53}BCl_2N_9Re$ (1096.0): C 61.60 (calc. 59.18); H 4.65 (4.87); N 10.66 (11.50); Cl 6.79 (6.47)%.

MS (FAB) (NBA, 35 °C): *m*/*z* = 1059.9 (M$^+$ − Cl), 938.2 (M$^+$ − BCl$_2$Ph). **IR** (KBr): ṽ = 2959 s, 2903 m, 1612 m, 1603 m, 1483 m, 1441 m, 1393 s, 1366 s, 1335 vs, 1281 m, 1258 m, 1200 m, 1150 m, 1090 s, 1051 m, 1024 m, 962 vw, 935 m, 831 m, 766 w, 754 m, 700 m, 671 w cm^{-1}. **UV/VIS** (CH_2Cl_2): λ = 371.5, 733.5 nm. **^{11}B NMR** (CD_2Cl_2): δ = 30 (decomposition product).

$^{t}Bu_{4}PcReNB(C_{6}F_{5})_{3}$ (**47**)

The reaction was conducted with 50.0 mg (0.053 mmol) of *t*Bu$_4$PcReN (**2**) and 27.3 mg (0.053 mmol) $B(C_6F_5)_3$. Yield: 77.2 mg (ca. 100 %), yellowish green solid. $C_{66}H_{48}BF_{15}N_9Re$ (1449.16): C 55.44 (calc. 54.70); H 3.14 (3.34); N 8.37 (8.70)%.

MS (FAB) (NBA, 50 °C): *m*/*z* = 937.3 (M$^+$ − B(C$_6$F$_5$)$_3$). **IR** (KBr): ṽ = 3448 w, 2964 m, 1642 m, 1614 m, 1515 s, 1468 vs, 1396 w, 1366 w, 1330 s, 1283 m, 1258 m, 1195 w, 1156 w, 1095 vs, 1052 w, 980 s, 936 m, 897 vw, 857 vw, 835 w, 794 vw, 758 w, 673 w cm^{-1}. **UV/VIS** (CH_2Cl_2): λ = 352.5, 681.5, 715.5 nm. **^{11}B NMR** (CD_2Cl_2, RT): δ = −6.50.

$^{t}Bu_{4}PcReNBPh_{3}$ (**48**)

The reaction was conducted with 20 mg (0.02 mmol) of *t*Bu$_4$PcReN (**2**) and 5.2 mg (0.02 mmol) BPh_3. Yield: 25.0 mg (99 %), bluish green solid.

MS (FAB) (NBA, 50 °C): *m*/*z* = 1102.4 (M$^+$ − Ph), 938.3 (M$^+$ − BPh$_3$). **IR** (KBr): ṽ = 2961 vs, 2903 w, 2864 w, 1614 w, 1483 m, 1437 m, 1393 m, 1364 m, 1331 vs, 1281 m, 1258 vs, 1202 w, 1148 m, 1092 vs, 1051 s, 1024 s, 935 w, 893 vw, 856 vw, 829 m, 802 m, 768 w, 754 m, 698 s, 669 w, 601 vw cm^{-1}. **UV/VIS** (CH_2Cl_2, glass plates): λ = 344.5, 664.0, 695.5 nm. **^{11}B NMR** (CD_2Cl_2): δ = 45.7 (decomposition product).

$^{t}Bu_{4}PcReNBEt_{3}$ (**49**)

The reaction was carried out with 20.0 mg (0.02 mmol) of *t*Bu$_4$PcReN (**2**) and 0.02 ml (0.02 mmol) of a 1 M BEt_3 solution (THF). Yield: 22.0 mg (ca. 100 %), bluish green solid.

MS (FAB): *m*/*z* = 1008.3 (M$^+$ + 2H − Et), 1006.3 (M$^+$ − Et), 937.3 (M$^+$ − BEt$_3$). **IR** (KBr): ṽ = 3213 s, 2963 s, 2905 vw, 1782 w, 1699 w, 1612 w, 1568 w, 1520 vs, 1479 vs, 1445 vs, 1396 vs, 1367 vs, 1350 s, 1331 s, 1281 w, 1259 s, 1196 s, 1092 s, 1049 s, 1024 m, 937 vw, 831 m, 804 s, 766 w, 754 m, 667 w cm^{-1}. **IR** (CH_2Cl_2): ṽ = 3055 w, 2988 w, 1421 w, 1265 vs, 1096 w, 1015 w, 897 w, 804 w, 743 vs, 706 vs cm^{-1}. **UV/VIS** (CH_2Cl_2, glass plates): λ = 341.5, 657.5, 696.0 nm. **^{11}B NMR** (CD_2Cl_2): δ = −0.2 (*t*Bu$_4$PcReN-BEt$_3$); 32.0, 55.3 (decomposition products).

$^{t}Bu_{4}PcReNAlCl_{3}$ (**50**)

The reaction was carried out in a solvent mixture of THF and CH_2Cl_2 with 30.0 mg (0.032 mmol) of *t*Bu$_4$PcReN (**2**) and 4.3 mg (0.032 mmol) of $AlCl_3$. Yield: 34.0 mg (99 %), green solid.

MS (FAB) (NBA, 30 °C): *m*/*z* = 938.4 (M$^+$ − AlCl$_3$). **IR** (KBr): ṽ = 3404 vs, 2962 vs, 1617 m, 1483 w, 1396 w, 1333 w, 1259 w, 1200 vw, 1096 m, 1052 w, 937 vw, 804 w, 754 vw, 668 w cm^{-1}. **UV/VIS** (CH_2Cl_2, glass plates): λ = 366.0, 696.0 nm.

$^{t}Bu_{4}PcReNGaCl_{3}$ (**51**)

The reaction was carried out in a mixture of hexane, CH_2Cl_2 and THF with 80.0 mg (0.085 mmol) of *t*Bu$_4$PcReN (**2**) and 15.0 mg (0.085 mmol) of $GaCl_3$. Yield: 94.5 mg (ca. 100 %), green solid. $C_{48}H_{48}Cl_3GaN_9Re$ (1113.3): C 51.60 (calc. 51.79); H 4.62 (4.35); N 10.66 (11.32)%.

MS (FAB) (NBA, 50 °C): *m*/*z* = 938.4 (M$^+$ − GaCl$_3$+H). **IR** (KBr): ṽ = 3448 m, 2960 s, 2866 m, 1612 s, 1482 s, 1395 s, 1365 s, 1331 vs, 1282 m, 1258 s, 1200 m, 1149 m, 1093 vs, 1051 s, 935 s, 833 s, 766 w, 754 s, 694 w, 670 m cm^{-1}. **UV/VIS** (CH_2Cl_2): λ = 350.5, 720.5 nm.

$^{t}Bu_{4}PcReNGaBr_{3}$ (**52**)

The reaction was carried out in a mixture of hexane and CH_2Cl_2 with 20.0 mg (0.021 mmol) of *t*Bu$_4$PcReN (**2**) and 6.6 mg (0.021 mmol) of $GaBr_3$. Yield: 26.2 mg (99 %), green solid.

MS (FAB) (NBA, 50 °C): *m/z* = 937.6 ($M^+ - GaBr_3$). **IR** (KBr): $\tilde{\nu}$ = 2964 s, 2866 m, 1522 m, 1261 vs, 1097 vs, 1022 vs, 864 m, 800 vs, 667 m cm^{-1}. **UV/VIS** (CH_2Cl_2): λ = 350.5, 691.0, 721.5 nm.

$^tBu_4PcReNInCl_3$ (**53**)

The reaction was carried out in a mixture of THF, CH_2Cl_2 and hexane with 30.0 mg (0.032 mmol) of tBu$_4$PcReN (**2**) and 7.1 mg (0.032 mmol) of $InCl_3$. Yield: 37.0 mg (ca. 100 %), green solid.

MS (FAB) (NBA, 50 °C): *m/z* = 938.4 ($M^+ - InCl_3 + H$). **IR** (KBr): $\tilde{\nu}$ = 3439 vs, 2962 s, 1611 m, 1481 w, 1393 w, 1332 m, 1260 vs, 1200 vw, 1095 vs, 1021 vs, 933 vw, 803 vs, 751 vw cm^{-1}. **UV/VIS** (CH_2Cl_2, glass plates): λ = 349.5, 694.5 nm.

$[^tBu_4PcReNSitBuMe_2]^+Cl^-$ (**54**)

The reaction was carried out in a mixture of CH_2Cl_2 and toluene with 20.0 mg (0.02 mmol) of tBu$_4$PcReN (**2**) and 3.2 mg (0.02 mmol) of tBuMe$_2$SiCl. Yield: 22.4 mg (ca. 100 %), dark green solid.

MS (FAB) (NBA, 50 °C): *m/z* = 938.6 ($M^+ - t$BuMe$_2$Si), 1053.4 (M^+). **IR** (KBr): $\tilde{\nu}$ = 3448 m, 2959 s, 1615 w, 1573 w, 1523 s, 1485 w, 1394 w, 1368 m, 1334 m, 1260 vs, 1194 vw, 1091 vs, 1049 vs, 935 vw, 802 s, 754 vw, 669 vw cm^{-1}. **UV/VIS** (toluene, glass plates): λ = 369.0, 666.0, 696.0, 725.5 nm.

3 Reduction of 9 with C_8K Followed by Reaction with Electrophiles

$(C_5H_{11})_8PcWNSi^tBuMe_2$ (**55**)

8.0 mg (0.060 mmol) of C_8K was added at room temperature to a solution of 43.0 mg (0.034 mmol) $(C_5H_{11})_8$PcWN (**9**) in 4 ml THF whence the solution became dark violet. After 3 h, 5.1 mg (0.034 mmol) of *tert.*-butyldimethylchlorsilane was added and the initial brownish-orange solution was left for 17 h when it changed it's colour to green. The solution was filtered, the solvent removed and the product extracted with hexane. Yield: 42.0 mg (89%), green solid.

MS (FD) (toluene, 30 °C): *m/z* = 1271.5 ($M^+ - Sit$BuMe$_2$). **IR** (KBr): $\tilde{\nu}$ = 2959 s, 2926 s, 2858 m, 1620 m, 1468 w, 1331 vw, 1261 s, 1090 s, 1028 m, 895 vw, 806 s cm^{-1}. **UV/VIS** (toluene): λ = 358.5, 725.5 nm. **UV/VIS** (THF): λ = 357.5, 723.0 nm. **^{1}H NMR** (THF-d_8): δ = 0.91 (9H, H-2), 1.02 (24H, H-8), 1.29 (6H, H-1),1.37 (16H, H-7), 1.61 (16H, H-6), 2.37 (16H, H-5), 2.72 (16H, H-4), 7.29-7.68 (8H, H-arom.).

$(C_5H_{11})_8PcWNGeMe_3$ (**56**)

8.0 mg (0.060 mmol) of C_8K was added to a solution of 43.0 mg (0.034 mmol) $(C_5H_{11})_8$PcWN (**9**) in 4 ml THF at room temperature with stirring. The dark red violet solution was stirred for 18 h. On adding 5.2 mg (0.034 mmol) trimethylgermanium chloride the colour of the solution turned to brownish-green. After 25 h a green solution was obtained which was filtered and the filtrate was evaporated. The residue was extracted with toluene. Yield: 40.0 mg (85%), green solid.

MS (FAB) (NBA, 30 °C): *m/z* = 1270.4 ($M^+ - GeMe_3$). **IR** (KBr): $\tilde{\nu}$ = 2963 m, 1262 vs, 1096 vs, 1020 vs, 864 m, 801 vs, 394 s cm^{-1}. **UV/VIS** (toluene): λ = 367.0, 731.5 nm. **^{1}H NMR** (THF-d_8): δ = 0.91 (24H, H-6), 1.29 (9H, H-1), 1.37 (16H, H-5), 1.59 (16H, H-4), 2.40 (16H, H-3), 2.72 (16H, H-2), 7.37-7.91 (8H, H-arom.). **^{13}C NMR (THF-d_8)**: δ = 13.3 (C-6), 20.45 (C-1), 22.4 (C-5), 30.6 (C-4), 31.7 (C-3), 32.8 (C-2), 123.2 (C-b), 127.1 (C-c), 129.2 (C-a), 147.5 (C-d).

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