Synthesis and Investigations on Nitrido(phthalocyaninato)rhenium Complexes

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The reactions of nitrido(tetra-*tert*-butylphthalocyaninato)rhenium (**1**) with boron tribromide leading to (tBu$_4$Pc)ReNBBr$_3$ (**4**) and with acetone to give the imido complex (tBu$_4$Pc)Re[NC(CH$_3$)$_2$CH$_2$C(O)CH$_3$]OH (**2b**) and its μ-oxo dimer **3** are reported. Starting from the corresponding 4,5-di-*n*-alkylphthalonitriles and ammonium perrhenate four soluble nitrido(octa-*n*-alkylphthalocyaninato)rhenium complexes **5–8** were synthesized. Nitrido(octa-*n*-pentylphthalocyaninato)rhenium (**6**) was treated with boron tribromide to afford [(C$_5$H$_{11}$)$_8$Pc]ReNBBr$_3$ (**9**).

To investigate the chemical and optoelectronic properties of hitherto unknown nitrido-bridged phthalocyaninato transition-metal/main-group complexes (PcMNPcM′: M = Re, Mo, W; M′ = Si, Ge, Sn) a suitable synthetic procedure was needed. The heavier transition-metal ions in high oxidation states, which are suitable to form the M−N triple bond, are used to prepare the nitrido complexes. N^{3-} (nitride) containing a triple bond is known as one of the strongest π-donor ligands.[1] Some (nitrido)metal complexes of porphyrins, e.g. (TPP)MnN,[2] (OEP)ReN[3] and others[4] have been prepared, some nitrido complexes with phthalocyanines are also known, namely PcMnN,[5] PcTcN,[6] PcReN[7] and the dinuclear complexes (PcFe)$_2$N[8] and (PcRu)$_2$N.[9] These nitrido(phthalocyaninato) complexes are practically all insoluble in organic solvents. Recently, we published the first soluble (phthalocyaninato)rhenium compound, (tBu$_4$Pc)ReN (**1**),[10] which exists in four structural isomers.

Here we report on the reaction of (tBu$_4$Pc)ReN (**1**) with boron tribromide leading to (tBu$_4$Pc)ReNBBr$_3$ (**4**) and the reaction of **1** with acetone to afford (tBu$_4$Pc)Re[NC(CH$_3$)$_2$CH$_2$C(O)CH$_3$]OH (**2b**) and {(tBu$_4$Pc)Re[NC(CH$_3$)$_2$CH$_2$C(O)CH$_3$]}$_2$O (**3**), which are the first μ-nitrido(phthalocyaninato) complexes between rhenium and boron or carbon, respectively. In addition we describe the synthesis of the octasubstituted (phthalocyaninato)rhenium complexes [(C$_4$H$_9$)$_8$Pc]ReN (**5**), [(C$_5$H$_{11}$)$_8$Pc]ReN (**6**), [(C$_6$H$_{13}$)$_8$Pc]ReN (**7**) and [(C$_7$H$_{15}$)$_8$Pc]ReN (**8**) and the reaction of **6** with BBr$_3$.

The reaction of a mixed-ligand nitridorhenium(V) complex, [ReN(Cl)(Me$_2$PhP)$_2$R$_2$tcb] [R$_2$tcb = *N*-(*N*,*N*-dialkylthiocarbamoyl)benzamidinate] with HCl and HBr in acetone to form a nitrene-like compound, Re[NC(CH$_3$)$_2$CH$_2$C(O)CH$_3$]X$_3$(Me$_2$PhP)$_2$ (X = Cl, Br) was recently described.[11] On addition of few drops of concentrated HCl to a suspension of tBu$_4$PcReN (**1**) in acetone a colour change from blue to blue-green occurs with dissolution of the solid. A UV/Vis spectrum of this solution exhibits broader bands with a red shift of the Q band of 30 nm relative to that of the starting material. The change in colour may be due to protonation of either the isoindoline nitrogen atoms of **1**[12] or the nitrido N atom. In the mechanism given in ref.[11], firstly the formation of diacetone alcohol due to the addition of HCl and secondly the attack of the nitrido nitrogen atom at the C−OH group are described. A direct way seemed more appropriate to us, namely a nucleophilic attack of the nitrido N atom to the carbonyl C atom of acetone to form **2a**, which reacts with a second molecule of acetone to form **2b** as shown in Scheme 1. This suggestion avoids the formation of diacetone alcohol in the first step which is very much dependent upon the acid concentration and temperature. After a reaction time of several days, the condensation product **2b** of diacetone alcohol and **1** was isolated (Scheme 1). For charge compensation, the *trans* position at the rhenium atom is occupied by OH$^-$. While purifying the crude product by column chromatography on aluminium oxide a small amount of the μ-oxo dimer {(tBu$_4$Pc)Re[NC(CH$_3$)$_2$CH$_2$C(O)CH$_3$]}$_2$O (**3**) is eluted (see below).

A comparison of the IR spectra of (tBu$_4$Pc)Re[NC(CH$_3$)$_2$CH$_2$C(O)CH$_3$]OH (**2b**) with that of (tBu$_4$Pc)ReN (**1**) reveals the disappearance of $\tilde{\nu}_{\mathrm{Re\equiv N}}$ = 978 cm^{-1} in **2b**, while additional bands at $\tilde{\nu}$ = 1123, 1148 and 3651 cm^{-1} appear. One of the two bands at $\tilde{\nu}$ = 1123 cm^{-1} and $\tilde{\nu}$ = 1148 cm^{-1} is assigned to the stretching vibration $\tilde{\nu}_{\mathrm{Re=N}}$.[1] There is no possible assignment for the origin of the other band. The C=O vibration of **2b** can be attributed to the band at $\tilde{\nu}_{\mathrm{C=O}}$ = 1718 cm^{-1}. A weak but sharp band at $\tilde{\nu}$ = 3651 cm^{-1} is caused by the OH group. The ^{1}H-NMR spectrum of **2b** shows, besides the expected signals for the *tert*-butyl protons (δ = 1.74−1.95) and the protons in the aromatic region (δ = 8.13 and 9.35), three groups of signals at δ = 0.14, −0.80 and −2.08 in the ratio 3:2:6. They are assigned to CH$_3$ in the neighbourhood of the carbonyl group, the CH$_2$ group and the equivalent CH$_3$ groups, respectively. The splitting of these groups is either caused by aggregation effects or is due to the four isomers

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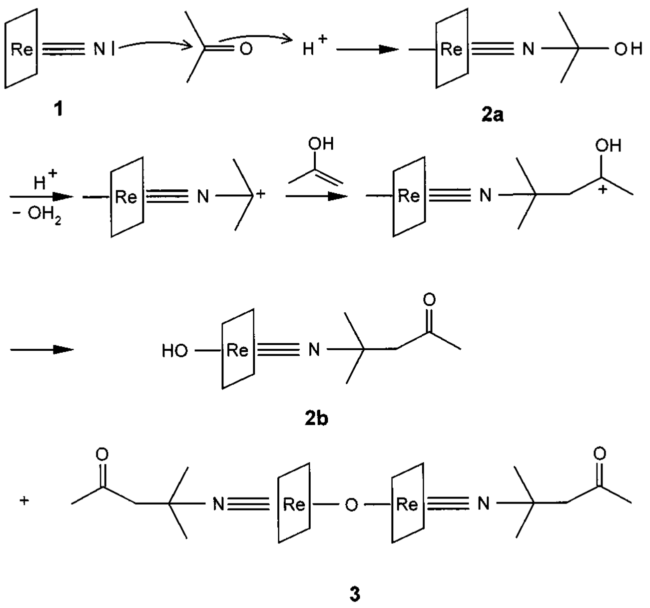


Scheme 1. Possible mechanism leading to **2b** and **3**

present in tetrasubstituted phthalocyanines.[13] The structure of **2b** is also proved by its ^{13}C-NMR spectrum. In addition to the signals already observed for **1**,[10] five signals for **2b** at δ = 202.07, 65.51, 47.40, 29.17 and 21.65 corresponding to the six C atoms of the axial ligand are observed.

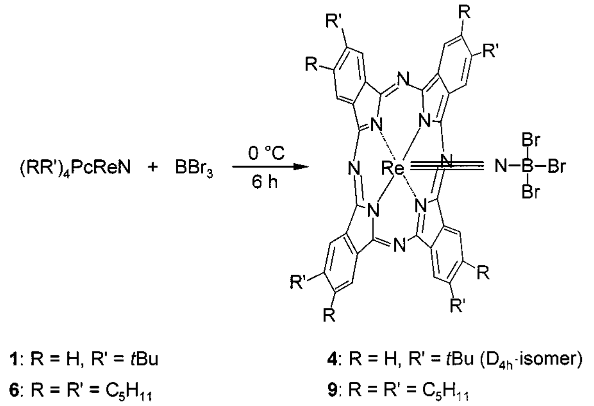
Besides some changes in intensity, the IR spectrum of **3** shows two new bands at $\tilde{\nu}$ = 727 and 802 $\mathrm{cm^{-1}}$, which cannot be assigned and consequently no O−H vibration $\tilde{\nu}$ = 3651 $\mathrm{cm^{-1}}$ was observed. Dimeric phthalocyanines with a coplanar arrangement of the macrocycles and an ideal D_{4h} symmetry show a blue shift of the Q band,[14] which is also observed in **3** by 37 nm relative to **1**. From this shift the exciton coupling can be estimated to be about 1600 $\mathrm{cm^{-1}}$, which is in accordance with the value for dimeric phthalocyanines.[14]

The ^{1}H-NMR spectrum of **3** exhibits in all regions sharp signals in the expected ratio of intensity. In the aromatic region several signals between δ = 9.46 and 8.20 are found besides signals due to the *tert*-butyl protons between δ = 2.63 and 2.05, which are attributed to the higher number of isomers. The low-field shift of the *tert*-butyl protons by about 0.5 ppm and the high-field shift of the protons of the axial imido ligand at δ = −0.63, −1.68 and −3.01 of about 0.7 to 1.0 in **3** are caused by the additional ring current of the second macrocycle.

The unsubstituted PcReN does not react with acetone/HCl even after several days. This is due to the poor solubility of PcReN.

(Nitrido)metal complexes are suitable precursors to complexes with nitrogen bridges between the transition-metal rhenium (M) and main-group elements such as, for example, boron (M′) (M≡N−M′). We investigated the possibility of a reaction of **1** and $(C_5H_{11})_8$PcReN (**6**) with BBr_3. Nitrogen-bridged rhenium−boron complexes like $Br_4ReNBBr_3$,[15a] $Re(NBCl_3)Cl_2[P(CH_3)_2C_6H_5]_3$[15b] and $(PEt_2C_6H_5)_3X_2ReNBY_3$ (X = Cl, Br; Y = F, Cl, Br)[15c] are known.

The reaction of (tBu$_4$Pc)ReN (**1**) with the Lewis acid BBr_3 in dichloromethane at 0°C for 6 h leads to a bonding of the boron atom to the axial nitrogen atom of **1** (Scheme 2). After removing the solvent and the excess of BBr_3 under vacuum, (tBu$_4$Pc)ReNBBr$_3$ (**4**) was obtained, which is sensitive to moisture.

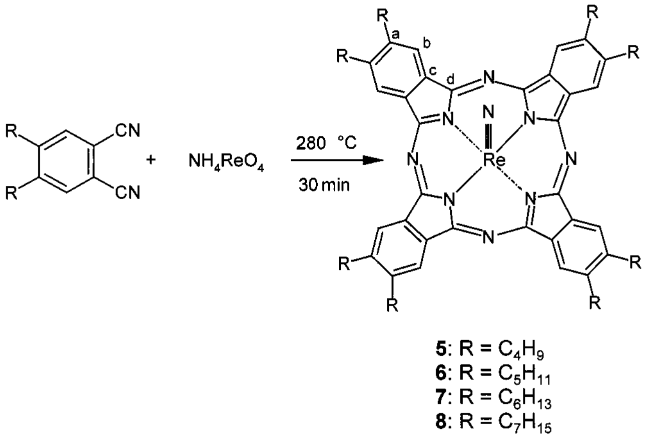


Scheme 2. Synthesis and Structure of (tBu$_4$Pc)ReNBBr$_3$ (**4**) and $[(C_5H_{11})_8Pc]ReNBBr_3$ (**9**)

In the FD MS and ionspray MS the M$^+$ peak of **4** was absent. However, (tBu$_4$Pc)ReNBBr$_2$, (tBu$_4$Pc)ReNBBr and BBr_3 were detected at m/z = 1107.5, 1029.6 and 250.8, respectively. The peak for **1** is also found in these spectra due to adventitious moisture present, which decomposes **4** to HBr, $B(OH)_3$ and **1**. The IR spectrum of **4** shows new vibrations compared to **1**. The Re−N triple bond vibration at $\tilde{\nu}_{Re\equiv N}$ = 978 $\mathrm{cm^{-1}}$ is shifted to 1196 $\mathrm{cm^{-1}}$. This band matches with the vibrations reported for a nitrido bridge between the rhenium and the boron atom, which is assigned at $\tilde{\nu}$ = 1170 and 1180 $\mathrm{cm^{-1}}$.[15b] This absorption at lower wavelength of $\tilde{\nu}_{Re\equiv N}$ is caused by the coupling with the B−N vibration of the presumably linear axis Re≡N−B.[15b] The extent of this coupling is lower than in complexes like Re≡N−C ($\tilde{\nu}_{Re\equiv N}$ = 1123 or 1148 $\mathrm{cm^{-1}}$ for **2b**) due to the higher frequency of $\tilde{\nu}_{N-C}$ relative to $\tilde{\nu}_{N-B}$. The latter appears at $\tilde{\nu}_{N-B}$ = 645 $\mathrm{cm^{-1}}$ and the BBr_3 stretching vibration at $\tilde{\nu}_{B-Br}$ = 671 $\mathrm{cm^{-1}}$. In general, the N−B vibrations are located between 650 and 780 $\mathrm{cm^{-1}}$.[16] The absorption at longer wavelength is due to the coupling with $\tilde{\nu}_{Re\equiv N}$. In the UV/Vis spectrum of **4** the Q band is red-shifted from λ = 697 to 725 nm due to the electron-withdrawing effect of the BBr_3 group. The band is broadened and shows a shoulder at λ = 755 nm. Furthermore, the ^{11}B-NMR spectrum of **4** gave unambiguous evidence for a boron−nitrogen bond. Relative to that of BBr_3 (δ = 38.15), the ^{11}B signal of (tBu$_4$Pc)ReNBBr$_3$ (**4**) is shifted to δ = −12.90 showing the influence of the aromatic Pc ring.

To improve the stability of nitrido-bridged (phthalocyaninato)rhenium complexes and keep the good solubility we replaced the large *tert*-butyl groups by alkyl chains. Therefore the (octaalkylphthalocyaninato)rhenium complexes, $[(C_4H_9)_8Pc]$ReN (**5**), $[(C_5H_{11})_8Pc]$ReN (**6**), $[(C_6H_{13})_8Pc]$ReN

(**7**) and $[(C_7H_{15})_8Pc]ReN$ (**8**) were synthesized by treating the respective 4,5-di-*n*-alkylphthalodinitriles with ammonium perrhenate.[10] The phthalocyanines were purified by Soxhlet extraction with methanol followed by column chromatography with dichloromethane. The yields are lower than that of unsubstituted PcReN[17] but similar to the yield of (tBu$_4$Pc)ReN (**1**)[10] (Scheme 3).



Scheme 3. Synthesis and Structure of **5**−**8**

The IR spectra of **5**−**8** resemble other octa-*n*-alkyl-substituted (phthalocyanine)metal complexes[18] except in the region between 950 and 1000 cm^{-1}. A band of low intensity is observed in all IR spectra of **5**−**8**, which is assigned to the Re−N triple-bond stretching vibration.[1] These bands are in agreement with those found for PcReN[6] and (tBu$_4$Pc)ReN (**1**).[10] The UV/Vis spectra of the **5**−**8** show the Q band at λ = 705 nm (π-π^* transition) for **5** and vibronic transitions at λ = 673 and 633 nm (in toluene) [**6** (CH_2Cl_2): λ = 708, 676, 638; **7** (toluene): λ = 704, 671, 634; **8** (CH_2Cl_2): λ = 708, 676, 638]. The slight blue shift of the Q band in **5**,**7** relative to **6**,**8** is caused by the change of solvent. Compounds **5**−**8** show a red shift of the Q band of about 30 nm relative to that of other octasubstituted phthalocyanines.[18] This difference may be caused by the high oxidation state of rhenium (+V). Similarly for (tBu$_4$Pc)ReN (**1**), the Q band is red-shifted by about 25 nm to λ = 697 nm.[10][20] We have no indication for exciton interaction of dimers or even larger aggregates,[21] so monomeric units of **5**−**8** were assumed in solution. The B band of **5**−**8** shows two maxima for **5** at λ = 369 and 351 nm [**6** (CH_2Cl_2): 361, 347 nm; **7** (toluene): 369, 350 nm; **8** (CH_2Cl_2): 361, 347 nm]. The FD MS spectra of **5**−**8** exhibit the expected peaks at 1161.5 (**5**; M^+), 1274.0 (**6**; M^+), 1385.7 (**7**; M^+) and 1498.3 (**8**; M^+) showing all the calculated isotope distribution. A singlet at low field in the ^{1}H-NMR spectrum of **5**−**8** is due to their high symmetry: For **5** this signal appears at δ = 9.21, at δ = 8.75 for **6**, at δ = 8.81 for **7** and at δ = 9.13 for **8** and is assigned to the eight aromatic protons. For **1**[10] three multiplets are found in the aromatic region due to the four isomers of tetrasubstituted phthalocyanines (C_{4h}, C_{2v}, D_{2h}, C_s) at δ = 8.39, 9.46, and 9.56 in the ratio of 1:1:1. The alkyl chains in **5**−**8** show the usual and expected signals at higher field. The methyl groups appear as triplets with coupling constants J = 7.04 Hz for **5**, 7.08 Hz for **6**, 6.88 Hz for **7** and 6.71 Hz for **8** (Figure 1). In the ^{13}C-NMR spectra of **5**−**8** four signals in the aromatic region for the carbon atoms C-a [144.28 (**8**)−144.08 (**6**)], C-b [122.84 (**5**)−122.66 (**6**)], C-c [135.12 (**8**)−134.98 (**6**)] and C-d [148.30 (**8**)−148.04 (**6**)] are observed. This pattern matches well with other octasubstituted phthalocyanines.[18] However, (tBu$_4$Pc)ReN (**1**) shows ten signals at lower field, which are all split or show at least a shoulder due to its structural isomers.[10] In the higher field between δ = 34.13 and 14.19 the expected number of signals for alkyl carbon atoms for compounds **5**−**8** are found (Figure 1).

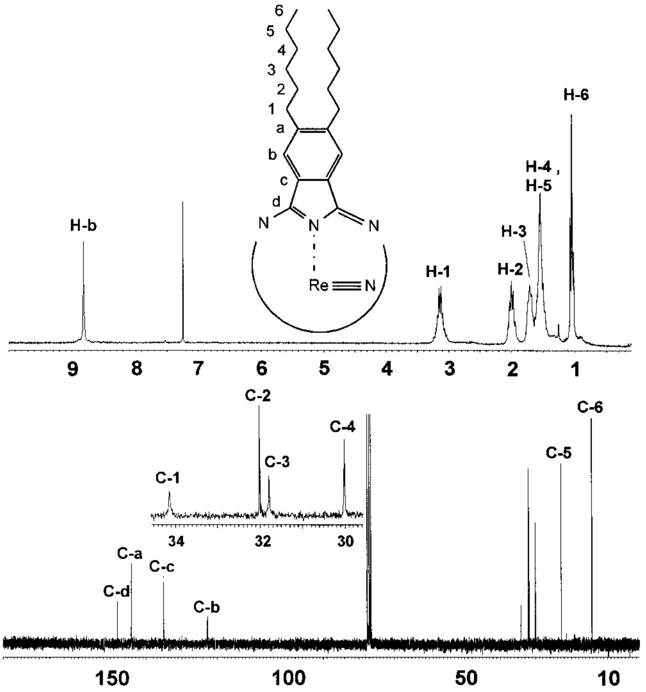


Figure 1. ^{1}H-and ^{13}C-NMR of $(C_6H_{13})_8PcReN$ (**7**)

The solubility of **5**−**8** is good in common organic solvents (e.g. $CHCl_3$, toluene, THF, pyridine), but less than that of (tBu$_4$Pc)ReN (**1**). The solubility increases from $[(C_4H_9)_8Pc]ReN$ (**5**) to $[(C_7H_{15})_8Pc]ReN$ (**8**). However, they are quite insoluble in hexane, methanol and diethyl ether.

$[(C_5H_{11})_8Pc]ReN$ (**6**) was treated with BBr_3 under the same conditions as for **4** to investigate the stability of the formed complex $[(C_5H_{11})_8Pc]ReNBBr_3$ (**9**) (Scheme 2). Compound **9** is less sensitive to moisture than **4** and hence it was possible to obtain the M^+ peak in the FAB MS at 1531.5 (M^+ + matrix) proving the higher stability of **9**. Peaks at 1450.4, 1372.4, 1286.5 and 1273.6 for $[(C_5H_{11})_8Pc]ReNBBr_2$, $[(C_5H_{11})_8Pc]ReNBBr$, $[(C_5H_{11})_8Pc]ReNB$ and $[(C_5H_{11})_8Pc]ReN$ (**6**) have been also observed. The Re−N triple-bond stretching vibration in the IR spectrum of **9** is found in the expected region similar to that of **4** at $\tilde{\nu}_{Re\equiv N}$ = 1194 cm^{-1}. Furthermore, the vibrations of $\tilde{\nu}_{B-Br}$ = 677 cm^{-1}, $\tilde{\nu}_{N-B}$ = 650 cm^{-1} and the usual vibrations for octasubstituted phthalocyanines give definite evidence for the suggested structure of **9**. The Q band in the UV/Vis spectrum of **9** is broadened and red-shifted to λ = 738 nm. The extent of this shift (30 nm) is the same as for (tBu$_4$Pc)ReNBBr$_3$ (**4**). The vibronic transitions at λ = 676 and 638 nm in **6** are also red-shifted to λ = 701.5 and 667.5 nm, respectively, due to the electron-withdrawing effect of the BBr$_3$ group, which is in accordance with **4**. In the same way the B band exhibits its maximum at λ = 380 nm. The ^{11}B-NMR spectrum of **9** shows a signal at δ = −12.75, similar to the one observed for **4** (δ = −12.90).

Experimental Section

4,5-Di-*n*-alkylphthalodinitriles were synthesized according to ref.[18] NH$_4$ReO$_4$ was prepared from Re metal,[21] which was a gift from Degussa AG. The solvents were purified by known procedures. − FT IR: Bruker IFS 48. − UV/Vis: Shimadzu UV−365. − MS: Varian Mat 711 (EI, FD). − ^{1}H, ^{13}C, ^{11}B NMR: Bruker AC 250 (^{1}H: 250.133 MHz; ^{13}C: 62.902; ^{11}B: 80.251). − Elemental analyses: Carlo Erba Elemental Analyser 1104, 1106.

(tBu$_4$Pc)Re[NC(CH$_3$)$_2$CH$_2$C(O)CH$_3$]OH (2b) and {tBu$_4$PcRe-[NC(CH$_3$)$_2$CH$_2$C(O)CH$_3$]}$_2$O (3): (tBu$_4$Pc)ReN (**1**)[10] (97 mg, 0.1 mmol) was suspended in 10 mL of acetone and treated with 5 drops of conc. HCl leading to dissolution and change of colour from blue to blue-green. After stirring at room temperature for 4 d in the dark, the solvent was removed and the residue chromatographed on Al$_2$O$_3$ with toluene as eluent to eliminate unchanged **1**. Two blue-green compounds were eluted with CH$_2$Cl$_2$ the first being the dimer **3** and the second the monomer **2b**. 59 mg (54%) of **2b** and 5 mg (2%) of **3**, both blue-green microcrystalline solids, were obtained.

2b: IR (KBr): ṽ = 3651 cm^{-1}, 3076, 2959, 2903, 2866, 1718, 1614, 1485, 1337, 1281, 1258, 1155, 1148, 1123, 1113, 1090, 1049, 935, 833, 768, 756. − UV/Vis (CH$_2$Cl$_2$): λ (lg ε) = 246 nm (4.70), 270 (4.54), 286 (4.47), 356 (4.79), 557 (3.06), 579 (3.58), 601 (3.83), 626 (4.40), 695 (5.08). − MS (FD); *m/z* (%): 1053.4 (100) [M$^+$]. − ^{1}H NMR (CDCl$_3$): δ = −2.13 to −2.08 [m, 6 H, C(C*H*$_3$)$_2$], 0.80 (m, 2 H, C*H*$_2$), 0.11−0.14 [m, 3 H, C(O)C*H*$_3$], 1.74−1.94 (m, 36 H, *t*Bu), 8.13−9.31 (m, 8 H, aromatic H). − ^{13}C NMR (CDCl$_3$): δ = 21.65 [m, C(*C*H$_3$)$_2$], 29.17 [m, C(O)*C*H$_3$], 31.90−32.18 [m, C(*C*H$_3$)], 36.04−36.14 [m, *C*(CH$_3$)$_3$], 47.70 (m, *C*H$_2$), 65.51 [m, *C*(CH$_3$)$_2$], 119.30−119.40 (m, *C*H$_2$), 122.90 (m, C-b), 127.95 (m, C-a), 135.14−135.30 (m, C-c), 137.78−138.00 (s, C-c′), 147.05−147.75 (m, C-d, C-d′), 153.61−153.78 (m, C-a′), 202.07 (C-O). − C$_{54}$H$_{60}$N$_9$O$_2$Re (1053.3): calcd. C 61.58, H 5.74, N 11.97; found C 61.43, H 5.54, N 11.65.

3: IR (KBr): ṽ = 3071 cm^{-1}, 2961, 2924, 2866, 1709, 1616, 1485, 1259, 1144, 1122, 1090, 802, 727. − UV/Vis (CH$_2$Cl$_2$): λ (lg ε) = 257 nm (4.65), 289 (4.48), 340 (4.48), 353 (4.52), 554 (3.50), 575 (3.57), 603 (3.91), 634 (4.14), 659 (4.85). − MS (FD); *m/z* (%): 2088.6 (100) [M$^+$]. − ^{1}H NMR (CDCl$_3$): δ = −3.03 to −2.95 [m, 12 H, 2 × C(C*H*$_3$)$_2$], −1.73 to −1.64 (m, 4 H, 2 × C*H*$_2$), −0.66−0.63 [m, 6 H, 2 × C(O)C*H*$_3$], 1.99−2.21 (m, 72 H, *t*Bu), 8.20−9.37 (m, 24 H, aromatic H). − ^{13}C NMR (H/C COSY; CDCl$_3$): δ = 22.26 [m, C(*C*H$_3$)$_2$], 29.65 [m, C(O)*C*H$_3$], 33.65 [m, C(*C*H$_3$)], 49.39 (m, *C*H$_2$), 119.89 (m, C-b′), 124.36 (m, C-b), 128.23. − C$_{108}$H$_{118}$N$_{18}$O$_3$Re$_2$ (2088.7): calcd. C 62.11, H 5.69, N 12.07; found C 64.86, H 6.88, N 9.17.

(tBu$_4$Pc)ReNBBr$_3$ (4) and [(C$_5$H$_{11}$)$_8$Pc]ReNBBr$_3$ (9): 0.053 mmol of the nitrido(phthalocyaninato)rhenium complexes (**1**,**6**)[10] was dissolved in 10 mL of CH$_2$Cl$_2$. Then 0.1 mL (1 mmol) BBr$_3$ was added dropwise at 0°C showing a change of colour from blue to green. The temperature was maintained for 6 h. Removal of the solvent and excess BBr$_3$ under vacuum gave 62.9 mg (100%) **4**, and 80.7 mg (100%) **9**, dark-green microcrystalline solids.

4: IR (KBr): ṽ = 3221 cm^{-1}, 2961, 2905, 1612, 1481, 1408, 1366, 1331, 1283, 1257, 1196, 1155, 1092, 1051, 935, 833, 810, 766, 754, 671, 645. − UV/Vis (CH$_2$Cl$_2$): λ = 382 nm, 725, 775. − MS (FD); *m/z* (%): 1107.5 (5) [M$^+$ − Br], 937.7 (100) [M$^+$ − BBr$_3$], 921.8 (35) [M$^+$ − NBBr$_3$]. − MS (ionspray); *m/z* (%): 1029.6 (100) [M$^+$ − 2 × Br], 938.4 (80) [M$^+$ − BBr$_3$], 378.2 (10) [ReNBBr$_2$], 294.6 (57) [ReNBBr$_3$], 250.8 (69) [BBr$_3$] − ^{11}B NMR (CDCl$_3$/BF3·Et2O): δ = −12.90 (s, 1B).

9: IR (KBr): ṽ = 3215 cm^{-1}, 2955, 1616, 1456, 1337, 1259, 1194, 1109, 1036, 883, 804, 754, 735, 677, 650. − UV/Vis (CH$_2$Cl$_2$): λ = 380 nm, 668, 702, 738. − MS (FAB); *m/z* (%): 1531.5 (3) [M$^+$ + matrix], 1450.4 (4) [M$^+$ − Br + matrix], 1372.4 (7) [M$^+$ − 2 × Br + matrix], 1286.5 (18) [M$^+$ − 3 × Br + matrix], 1273.6 (100) [M$^+$ − BBr$_3$]. − ^{11}B NMR (CDCl$_3$/BF3·Et2O): δ = −12.75 (s, 1 B).

Nitrido(octa-*n*-alkylphthalocyaninato)rhenium(V) [(R$_8$Pc)ReN] 5−8: 0.21 mmol of the appropriate 4,5-di-*n*-alkylphthalodinitriles was heated with 0.048 mmol NH$_4$ReO$_4$ to 280°C for 30 min. After cooling, the dark green reaction mixture was first chromatographed on Al$_2$O$_3$ (neutral, 10% H$_2$O) with dichloromethane as eluent (2 ×) to remove most of the impurities. Then the excess of dinitrile was extracted with methanol for 12 h by using a Soxhlet apparatus. 55 mg (5%) of **5,** 65 mg (5%) of **6**, 55 mg (4%) of **7** and 60 mg (4%) of **8** were obtained as dark green powders.

5: IR (KBr): ṽ = 2957 cm^{-1}, 2930, 1620, 1497, 1456, 1403, 1335, 1113, 1082, 1030, 964, 905, 754, 733. − UV/Vis (toluene): λ = 351 nm, 369, 633, 673, 705. − MS (FD); *m/z* (%): 1161.5 (100) [M$^+$]. − ^{1}H NMR (CDCl$_3$): δ = 1.18 (t, J = 7.04 Hz, 24 H, C*H*$_3$), 1.63−1.81 (m, 16 H, CH$_3$C*H*$_2$), 1.87−2.09 (m, 16 H, CH$_3$CH$_2$C*H*$_2$), 3.04−3.27 (m, 16 H, ArC*H*$_2$), 8.91 (s, 8 H, aromatic H). − ^{13}C NMR (CDCl$_3$): δ = 14.25 (s, *C*H$_3$), 23.35 (s, CH$_3$*C*H$_2$), 33.81 (s, CH$_3$CH$_2$*C*H$_2$), 33.91 (s, Ar*C*H$_2$), 122.84 (s, C-b), 135.11 (s, C-c), 144.22 (s, C-a), 148.27 (s, C-d). − C$_{64}$H$_{72}$N$_9$Re (1161.6): calcd. C 66.18, H 6.94, N 10.85; found C 66.39, H 6.53, N 10.45.

6: IR (KBr): ṽ = 2954 cm^{-1}, 2927, 2868, 1618, 1498, 1456, 1406, 1337, 1110, 1079, 1018, 965, 891, 754, 732. − UV/Vis (CH$_2$Cl$_2$): λ = 347 nm, 361, 638, 676, 708. − MS (FD); *m/z* (%): 1274.0 (100) [M$^+$]. − ^{1}H NMR (CDCl$_3$): δ = 1.11 (t, J = 7.08 Hz, 24 H, C*H*$_3$), 1.51−1.78 (m, 32 H, CH$_3$C*H*$_2$C*H*$_2$), 1.90−2.10 (m, 16 H, ArCH$_2$C*H*$_2$), 2.98−3.22 (m, 16 H, ArC*H*$_2$), 8.75 (s, 8 H, aromatic H). − ^{13}C NMR (CDCl$_3$): δ = 14.29 (s, *C*H$_3$), 22.83 (s, CH$_3$*C*H$_2$), 31.46 (s, CH$_3$CH$_2$*C*H$_2$), 32.52 (s, ArCH$_2$*C*H$_2$), 34.07 (s, Ar*C*H$_2$), 122.66 (s, C-b), 134.98 (s, C-c), 144.08 (s, C-a), 148.04 (s, C-d). − C$_{72}$H$_{96}$N$_9$Re (1273.8): calcd. C 67.89, H 7.60, N 9.90; found C 66.66, H 7.87, N 8.65.

7: IR (KBr): ṽ = 2955 cm^{-1}, 2926, 1618, 1496, 1456, 1406, 1337, 1109, 1080, 1024, 964, 900, 802, 754, 731. − UV/Vis (toluene): λ = 350 nm, 369, 634, 671, 704. − MS (FD); *m/z* (%): 1385.7 (100) [M$^+$]. − ^{1}H NMR (CDCl$_3$): δ = 1.04 (t, J = 6.88 Hz, 24 H, C*H*$_3$), 1.45−1.61 (m, 32 H, CH$_3$C*H*$_2$C*H*$_2$), 1.65−1.75 (m, 16 H, ArCH$_2$CH$_2$C*H*$_2$), 1.91−2.07 (m, 16 H, ArCH$_2$C*H*$_2$), 3.02−3.24 (m, 16 H, ArC*H*$_2$), 8.81 (s, 8 H, aromatic H). − ^{13}C NMR (CDCl$_3$): δ = 14.25 (s, *C*H$_3$), 22.88 (s, CH$_3$*C*H$_2$), 30.01 (s, CH$_3$CH$_2$*C*H$_2$), 31.79 (s, ArCH$_2$CH$_2$*C*H$_2$), 32.01 (s, ArCH$_2$*C*H$_2$), 34.13 (s, Ar*C*H$_2$), 122.75 (s, C-b), 135.04 (s, C-c), 144.14 (s, C-a), 148.10 (s, C-d). − C$_{80}$H$_{112}$N$_9$Re (1386.0): calcd. C 69.33, H 8.14, N 9.10; found C 70.27, H 8.17, N 8.91.

8: IR (KBr): ṽ = 2956 cm^{-1}, 2925, 1619, 1497, 1456, 1405, 1387, 1112, 1080, 1027, 977, 887, 752, 730. − UV/Vis (CH$_2$Cl$_2$): λ =

347 nm, 361, 638, 676, 708. − MS (FD); *m/z* (%): 1498.3 (100) [M^+]. − ^1H NMR ($CDCl_3$): δ = 0.98 (t, *J* = 6.71 Hz, 24 H, $\mathrm{C}H_3$), 1.38−1.77 (m, 60 H, $\mathrm{CH_3C}H_2\mathrm{C}H_2\mathrm{C}H_2\mathrm{C}H_2$), 1.89−2.12 (m, 16 H, $\mathrm{ArCH_2C}H_2$), 3.01−3.27 (m, 16 H, $\mathrm{ArC}H_2$), 8.92 (s, 8 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 14.19 (s, $C\mathrm{H_3}$), 22.81 (s, $\mathrm{CH_3}C\mathrm{H_2}$), 29.44 (s, $\mathrm{CH_3CH_2}C\mathrm{H_2}$), 30.26 (s, $\mathrm{CH_3CH_2CH_2CH_2}C\mathrm{H_2}$), 31.84 (s, $\mathrm{ArCH_2CH_2}C\mathrm{H_2}$), 32.05 (s, $\mathrm{ArCH_2}C\mathrm{H_2}$), 34.12 (s, $\mathrm{Ar}C\mathrm{H_2}$), 122.80 (s, C-b), 135.12 (s, C-c), 144.28 (s, C-a), 148.30 (s, C-d). − $C_{88}H_{128}N_9Re$ (1498.3): calcd. C 70.49, H 8.61, N 8.41; found C 69.35, H 8.10, N 9.05.

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