Novel Nitrido- and Oxo(phthalocyaninato) Complexes of Molybdenum, Tungsten and Rhenium

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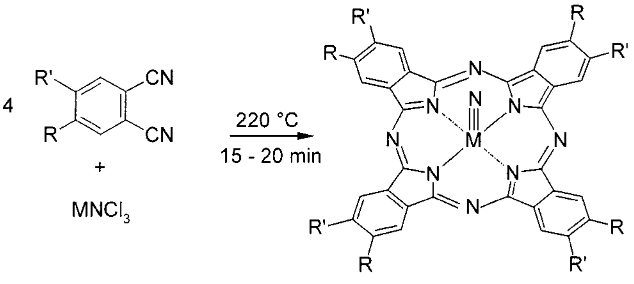
The synthesis of new nitrido(phthalocyaninato)molybdenum (**1**–**4**) and -tungsten complexes (**5**–**7**) starting from the corresponding phthalonitriles and $MNCl_3$ (M = Mo, W) is reported. In addition, the reaction of (tBu$_4$Pc)WN (**6**) with PPh_3 leading, after several steps, to the diamagnetic compound (tBu$_4$Pc)WO (**7**) is described. The reaction of (tBu$_4$Pc)ReN (**9**) with PPh_3 leads to [(tBu$_4$Pc)ReO]$_2$ (**12**), and of [$(C_5H_{11})_8$Pc]ReN (**10**) with PPh_3 leads, under different conditions, to {[$(C_5H_{11})_8$Pc]ReO}$_2$O (**11**).

Introduction

Continuing with our work on nitrido(phthalocyaninato)metal compounds[1] we report here on the synthesis and properties of novel nitrido(phthalocyaninato)metal complexes of molybdenum and tungsten, as well as two other oxo(phthalocyaninato)rhenium dimers. The aim of our work on the paramagnetic PcMN complexes (M = Mo, W) is to reduce them to the anionic phthalocyaninato complexes PcMN$^-$ and to investigate their subsequent reaction with electrophiles to obtain new nitrido-bridged phthalocyaninato complexes. These complexes should be more reactive in their nitrido functionality than the nitrido-bridged rhenium phthalocyanines which we have reported recently.[1]

Until now, the few publications concerning molybdenum phthalocyanines mostly concentrate on oxophthalocyaninatomolybdenum(IV), PcMoO.[2] Some porphyrinato complexes of molybdenum are known.[3] The most interesting are (TMP)MoN (TMP = tetramesitylporphyrinato), (TTP)MoN (TTP = tetratolylporphyrinato) and (TPP)MoN (TPP = tetraphenylporphyrinato) because the molybdenum is in the +5 oxidation state and in a planar arrangement with the porphyrinato ligand.[4]

The preparation of unsubstituted[5] and substituted PcMoN is successful starting from the appropriate phthalonitriles and $MoNCl_3$[6,7], by melting them at 220 °C for 15 to 20 minutes (Scheme 1). The dark green PcMoN (**1**) can be separated from its impurities by Soxhlet extraction with acetone and toluene. The substituted complexes (R_8Pc)MoN [R = C_3H_7 (**2**), C_4H_9 (**3**), C_5H_{11} (**4**)] are purified by column chromatography on Al_2O_3 with toluene and by washing with methanol. The yield is 65% in the case of **1**. The yields are higher for the substituted PcMoN complexes [**2** (11%), **3** (8%), **4** (10%)] than for the corresponding nitrido(phthalocyaninato)rhenium complexes.[1] We assume that either the excess dinitrile is responsible for the Cl radical abstraction from $MNCl_3$, or that Cl$^-$ is oxidized to Cl_2 with reduction of the metal center.



	1	2	3	4	5	6	7
M	Mo	Mo	Mo	Mo	W	W	W
R	H	C_3H_7	C_4H_9	C_5H_{11}	H	H	C_5H_{11}
R‘	H	C_3H_7	C_4H_9	C_5H_{11}	H	tBu	C_5H_{11}

Scheme 1. Synthesis and structure of nitrido(phthalocyaninato)metal complexes

The M$^+$ peak for PcMoN (**1**) in the FAB-MS is observed at m/z = 623.1 (calcd. 622.5). The complexes (R_8Pc)MoN [R = C_3H_7 (**2**), C_4H_9 (**3**), C_5H_{11} (**4**)] show their M$^+$ peak in the FD-MS with the expected isotopic pattern. The infrared spectra of **1**–**4** are difficult to interpret. Usually the Mo≡N stretching vibration[6] is observed higher than 1000 cm^{-1} and the Mo=O vibration in phthalocyanines appears at ṽ =

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Table 1. EPR, IR and UV data of the new phthalocyanines

	EPR g	IR [cm^{-1}] $\nu_{M\equiv N}$	UV [nm] λ (Q)
PcMoN (**1**)	1.97	953	703.5 (ClN)[a]
[(C_3H_7)$_8$Pc]MoN (**2**)	1.97	974	709.0 (toluene)
[(C_4H_9)$_8$Pc]MoN (**3**)	1.97	962	711.5 (toluene)
[(C_5H_{11})$_8$Pc]MoN (**4**)	1.97	974	716.0 (toluene)
PcWN (**5**)	1.88	953	751.0 (ClN)[a]
(*t*Bu$_4$Pc)WN (**6**)	1.89	959	745.0 (toluene)
[(C_5H_{11})$_8$Pc]WN (**7**)	1.89	957	770.5 (toluene)
PcWO (**8**)	–	$\nu_{W=O}$ = 1047[b]	674.5 (toluene)
[(*t*Bu$_4$Pc)Re(O)]$_2$ (**12**)	–	$\nu_{Re=O}$ = 960[b]	652.5 (chloroform)
{[(C_5H_{11})$_8$Pc]Re(O)}$_2$O (**11**)	–	–	701.5 (chloroform)

[a] ClN = 1-chloronaphthalene. – [b] Tentative assignment.

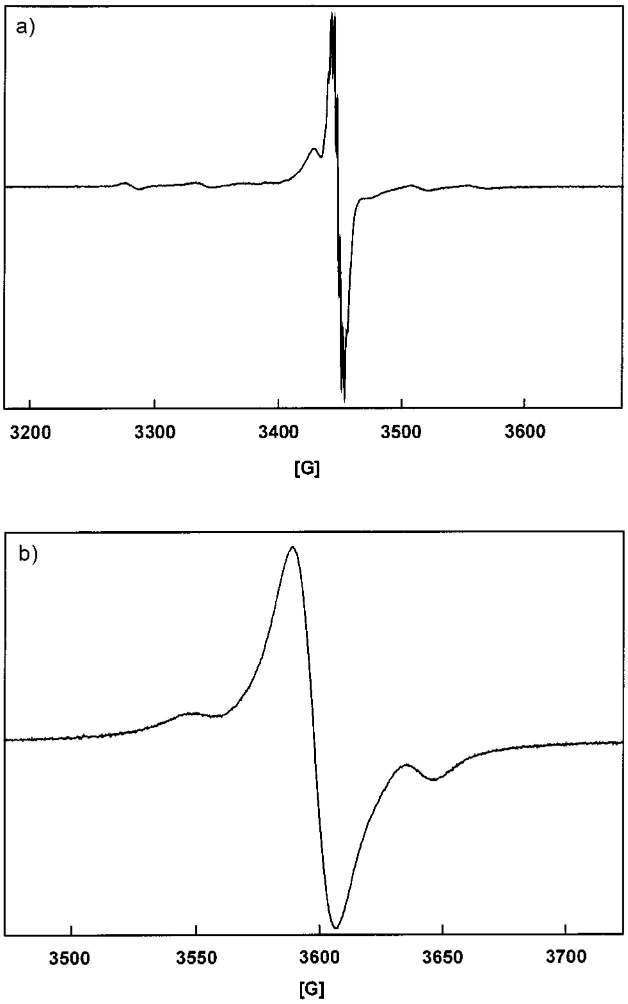


Figure 1. EPR spectra of a) PcMoN (**1**) and b) (C_5H_{11})$_8$PcWN (**7**)

950–980 cm^{-1}.[2a] For PcMoN (**1**) and (R$_8$Pc)MoN **2**–**4** the Mo≡N stretching vibration is observed below 1000 cm^{-1} (Table 1). The lowered value of the stretching vibration can be explained by interaction of the nitrogen lone pair with the following Lewis acidic Mo center within the same stack, which reduces the bond order of MoN. In PcReN the Re≡N stretching vibration is located at $\tilde{\nu}$ = 978 cm^{-1} due to the same effect.[1b,1c] This lowering is not unusual, e.g. in MoNF$_4^-$ the band for MoN is located at $\tilde{\nu}$ = 969 cm^{-1}.[8] The UV/Vis spectrum of **1** in solution and as a KBr pellet indicates the presence of dimers: the maximum of the Q-band in solution (chloroform) is seen at λ = 703.5 nm (satellites are located at λ = 639.5 and 602.5 nm) and a shoulder is seen at λ = 777.0 nm in the solution spectrum and at λ = 791.5 nm in the solid state. Under the assumption of a Davidov–Kasha exciton interaction,[9] the shoulders at λ = 649.5 and 791.5 nm are due to dimers with an interaction of ΔE = 2750 cm^{-1}. In contrast to **1** the UV/Vis spectra of **2**–**4** show the usual Q- and B-bands of monomeric phthalocyanines. As an element of group six, molybdenum in the oxidation state +5 has a d^1 configuration with one unpaired electron. An EPR spectrum of PcMoN (**1**) in 1-chloronaphthalene shows intense central lines (g = 1.97) due to the coupling of the electron with the five nitrogens. Six weaker lines seen symmetrically on both the right and the left side of the central signal are due to the electron–Mo^{95}/Mo^{97} coupling (Figure 1a). The simulated spectrum corresponds to the measured spectrum. The spectra of the more soluble compounds **2**–**4** show the same patterns (Table 1). The g factor for the complexes **1**–**4** is 1.97.

Some phthalocyaninato complexes of tungsten have been synthesized,[10] but only in PcWCl$_3$[10a] and (ClPc)W(O)OH[11] is the metal in the +5 oxidation state. These examples indicate that nitrido(phthalocyaninato)tungsten complexes should also exist. With the same synthetic strategy as for the PcMoN compounds, unsubstituted, tetra- and octasubstituted nitrido(phthalocyaninato)tungsten complexes **5**–**7** are obtained (Scheme 1). Their stability against moisture is greater than that observed for the molybdenum phthalocyanines **1**–**4**. PcWN (**5**) is separated from its impurities by Soxhlet extraction with ethanol, acetone and toluene and isolated as a dark green powder in high yield (70%). The M$^+$ peak of **5** in the FAB-MS appears at *m*/*z* = 709.9 (calcd. 710.1). Purification of (*t*Bu$_4$Pc)WN (**6**) and [(C_5H_{11})$_8$Pc]WN (**7**) is not possible by column chromatography. The excess of phthalonitrile in the substituted complexes **6** and **7** is separated by Soxhlet extraction (hexane), further impurities are precipitated with dichloromethane/hexane. The synthesis of (C_5H_{11})$_8$PcWN (**7**) can be carried out in a higher yield using W(NTos)$_2$Cl$_2$[12] instead of WNCl$_3$. Impurities are separated by washing the crude product with methanol and precipitated with dichloromethane/hexane. The molecular ions of compounds **6** and **7** can be seen in the FD-MS with the expected isotopic pattern. The IR spectrum of **5** is quite similar to that of PcReN[1b,1c] and almost the same as that of PcMoN (**1**). All phthalocyanine vibrations are in the usual regions. The W≡N vibration is expected between 1000 and 950 cm^{-1}. A band of medium intensity at $\tilde{\nu}$ = 953 cm^{-1} is assigned to this vibration (Figure 2). The W=O vibration in (ClPc)W(O)OH[11] is also found around $\tilde{\nu}$ = 953 cm^{-1}. This indicates that the W≡N vibration appears at lower wavelength due to the interaction with the next metal center within a stack as explained for PcMoN

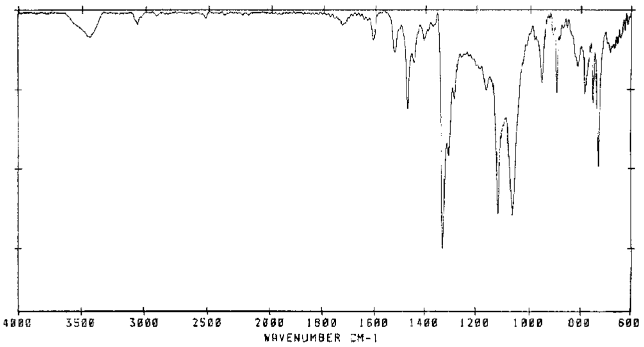


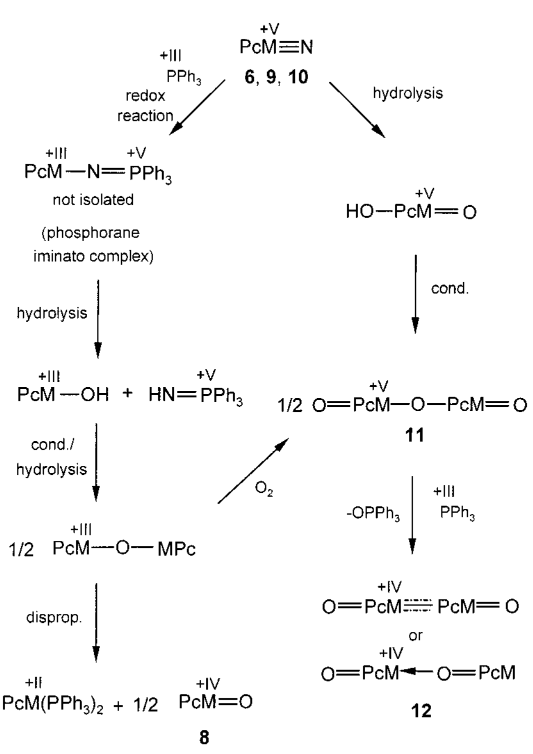
Figure 2. IR spectrum of PcWN (**5**)

(**1**). The W≡N vibration in the soluble complexes **6** and **7** is observed at $\tilde{\nu}$ = 959 (**6**) and 957 cm^{-1} (**7**) (Table 1).

In (ClPc)W(O)OH the maximum of the Q-band is at λ = 730 nm.[11] PcWN (**5**) shows a red shift in the Q-band maximum at λ = 751.0 nm (Table 1); the Q-band is broadened and shows two shoulders at λ = 699.5 and 673.5 nm. A shoulder at higher wavelength cannot be found, which indicates that only monomeric units of **5** are present in solution. (tBu$_4$Pc)WN (**6**) and [(C$_5$H$_{11}$)$_8$Pc]WN (**7**) show broadened Q-bands at λ = 745.0 (**6**) and 770.5 nm (**7**). The d^1-electron configuration of tungsten in PcWN (**5**), (tBu$_4$Pc)WN (**6**) and [(C$_5$H$_{11}$)$_8$Pc]WN (**7**) allows the recording of their EPR spectra. Compound **6** exhibits a broad intense signal at $g = 1.88$ without hyperfine structure due to the electron–nitrogen or electron–tungsten coupling (Table 1). This is quite normal for powder spectra even at 77 K.[11] However, **6** and **7** show an electron–W^{183} coupling in toluene solution (Figure 1b). Two signals, besides the main resonance, with an intensity of about 7% appear [g = 1.89 (**6**, **7**)] (Table 1).

Reactions of PcReN[13] and PcMoO[2f] complexes with phosphanes have been the focus of recent studies. To date, the exact mechanism of the reaction of the PcMN complexes **6**, (tBu$_4$Pc)ReN (**9**), [(C$_5$H$_{11}$)$_8$Pc]ReN (**10**) with PPh$_3$ is unknown but we suggest two pathways (Scheme 2). The first possible mechanism involves nucleophilic attack of the phosphane at the LUMO of the nitrido complex having mainly the character of an MN–π*-orbital.[6] This redox reaction would lead to a phosphorane iminato complex that could undergo hydrolysis to finally yield PcWO (**8**) as described in Scheme 2. The second pathway begins with hydrolysis of **6**, **9** and **10**. After condensation **11** is obtained which can be reduced with PPh$_3$ to the phthalocyaninatometal complex **12**.

As a first attempt the reaction of (tBu$_4$Pc)WN (**6**) with PPh$_3$ was investigated. After column chromatography only (tBu$_4$Pc)WO (**8**) was isolated in 50% yield. The FD-MS spectrum of **8** shows the expected molecular peak at m/z = 936.5 (calcd. 936.3) in accordance with the calculated isotopic pattern. An interesting result is indicated in the IR spectrum of **8** in which the W≡N stretching vibration disappears. All other vibrations show very little or no difference in intensity or wave number. The assignment of the W=O vibration is difficult, however a shoulder at $\tilde{\nu}$ = 1047 cm^{-1} could correspond to this vibration (Table 1). In the UV/Vis spectrum of **8** the Q-band shows a heavy blue shift relative to (tBu$_4$Pc)WN (**6**), with a maximum at λ = 674.5 nm and shoulders at λ = 725.0 and 611.0 nm (Table 1). In the same way the B-band is shifted to lower wavelength. The ^{1}H NMR spectrum of diamagnetic (tBu$_4$Pc)WO (**8**) shows the signals of the tBu groups between δ = 1.60–2.26 due to the structural isomers present in tetrasubstituted phthalocyanines. The signals of the aromatic protons are found between δ = 7.5–8.6.



Scheme 2. Mechanism leading to PcWO (**8**), [tBu$_4$PcRe(O)]$_2$ (**12**) and [(C$_5$H$_{11}$)$_8$PcRe(O)]$_2$O (**11**)

The reaction of PcMN with PPh$_3$ is studied further with the nitridophthalocyaninatorhenium complexes (tBu$_4$Pc)ReN (**9**) and [(C$_5$H$_{11}$)$_8$Pc]ReN (**10**). Recently the reaction of Re$_2$O$_7$ and phthalonitrile with PPh$_3$ leading to the formation of (PcRe)$_2$ was reported.[14] In the first step of this reaction (PPh$_3$)$_2$PcRe was formed, after heating to 350 °C (PcRe)$_2$ was obtained. (PPh$_3$)$_2$PcRe was also successfully prepared starting from "PcReO" and PPh$_3$.[13] The reaction of **9** and **10** with PPh$_3$ at different reaction temperatures gives different products (Scheme 2). At lower temperatures μ-oxo[oxoocta(n-pentyl)phthalocyaninato]rhenium {[(C$_5$H$_{11}$)$_8$Pc]Re(O)}$_2$O (**11**) is obtained, while at higher temperatures (350 °C) rhenium is reduced to the +4 oxidation state. After column chromatography on Al$_2$O$_3$ with toluene and dichloromethane as eluents, [(tBu$_4$Pc)Re(O)]$_2$ (**12**) is isolated. There are two possible structures for **12**: first, the stacking of a second molecule in trans-position to form a μ-oxo bridged dimer, and second a dimer with a rhenium-rhenium bond. From the UV/Vis spectra we assume that the dimeric complex [(tBu$_4$Pc)Re(O)]$_2$ (**12**) with a rhenium–rhenium bond is obtained. In the FD-MS the molecular peak for **12** is found at *m*/*z* = 1876.6 (calcd. 1876.4) and the signal of the monomeric fragment (tBu$_4$Pc)Re(O)$^+$ appears at *m*/*z* = 938.2. The IR spectrum of **12** shows differences from that of the starting material (tBu$_4$Pc)ReN (**9**). The Re≡N vibration disappears; however, the Re=O vibration is not seen due to strong new ligand vibrations in that region. In the UV/Vis spectrum of **12** in chloroform the dimerization is proved by the blue shift of the Q-band to λ = 652.5 nm relative to (tBu$_4$Pc)ReN (**9**) [λ_{max} (Q) = 698 nm (CH_2Cl_2)] and the appearance of the forbidden Q^--band at λ = 801.5 nm (Figure 3a, Table 1). The exciton interaction is calculated to be ΔE = 2850 cm^{-1}, while for (PcRe)$_2$ the calculated value is lower than 2400 cm^{-1}.[14] The interaction caused by the distance of the macrocycles is dependent on the radius of the metal ions. In (PcRe)$_2$ the oxidation state of rhenium is +2, but in **12** it is +4. The effect of the sterically demanding *t*Bu groups on the distance of the macrocycles is low.[15] With the UV/Vis spectrum as KBr pellet the exciton interaction in the solid state is ascertained to be ΔE = 2000 cm^{-1}. A higher distance of the macrocycles is concluded from these results and may be explained by an eclipsed conformation in the solid state. In solution, **12** rotates to the staggered conformation. A change of conformation was also established for (PcRe)$_2$.[14] In the presence of light, a chloroform solution of **12** decomposes as seen by the appearance of a greater absorbance of the monomer band at λ = 692.0 nm.

In the ^{1}H NMR spectrum of [(tBu$_4$Pc)Re(O)]$_2$ (**12**) a broadening of the signals due to the interaction of two macrocycles and the structural isomers is seen. The signals of the aromatic protons are between δ = 9.58–9.49 and δ = 8.50–8.39, while the *t*Bu groups are shifted to lower field (δ = 2.15–1.81) than for (tBu$_4$Pc)ReN (**9**).

The reaction of [(C_5H_{11})$_8$Pc]ReN (**10**) with PPh_3 at 250 °C for 30 minutes leads to the μ-oxo dimer [{(C_5H_{11})$_8$Pc}Re(O)]$_2$O (**11**) as a product of hydrolysis (Scheme 2). Compound **11** is separated from its impurities by column chromatography on Al_2O_3. Unchanged **10** is first obtained with toluene and **11** is then eluted with dichloromethane in 18% yield. The shorter reaction time at lower temperature does not reduce the rhenium. The mechanism of the reaction is still unknown but a suggested mechanism can be seen in Scheme 2. The calculated and observed isotopic pattern of the molecular peak at *m*/*z* = 2568.2 in the FD-MS are in agreement.

In the IR spectrum **11** shows two new intense bands at $\tilde{\nu}$ = 685 and 658 cm^{-1}. The Re≡N vibration disappears with the formation of a new band at $\tilde{\nu}$ = 802 cm^{-1}. There are different possibilities of a $M_2O_3^{4+}$ unit, e.g. (TTP)Nb_2O_3 has three μ-oxo-bridges.[16] This is not the case for **11** because in (tBu$_4$Pc)Re(O)OEt the Re=O vibration is assigned to $\tilde{\nu}$ = 949 cm^{-1}.[15] The O=PcRe–O–PcRe=O units in phthalocyanines are in a linear arrangement due to steric reasons. In linear complexes the Re–O–Re vibration is located between 650–700 cm^{-1}. In [(OEP)ReO]$_2$O (OEP = octaethylporphyrinato) this vibration is observed at $\tilde{\nu}$ = 675 cm^{-1}.[17] Consequently the new band at 802 cm^{-1} is assigned to a ligand vibration. The Re=O vibration is not found in the expected region due to strong bands at $\tilde{\nu}$ = 685 and 658 cm^{-1}. Another possible explanation for the new bands is that in a linear arrangement of O=PcRe–O–PcRe=O, vibrational coupling of the $\nu_{Re=O}$ and ν_{Re-O} modes may occur shifting $\nu_{Re=O}$ to lower (802 cm^{-1}) and ν_{Re-O} to higher frequencies (685/658 cm^{-1}). Dimerization is again confirmed by the UV/Vis spectrum of **11** in chloroform (Figure 3c). A red shift in the Q-band to λ = 701.5 nm is seen and the forbidden Q^--band is located at λ = 778.5 nm (Table 1). From these data the exciton interaction is estimated to be ΔE = 1410 cm^{-1}, in the solid state it is calculated to be ΔE = 1450 cm^{-1}. The appearance of the Q^--band may be explained by a lowering of symmetry. These results indicate that the conformation of **11** has not changed. In the ^{1}H NMR and the ^{13}C-DEPT-135 NMR spectra all expected signals are observed. The 16 equivalent aromatic protons show a singlet at δ = 8.80. The signals of the different methylene groups appear separate and are easily assigned. The methyl group shows its resonance as a triplet at δ = 1.20. In the ^{13}C-DEPT-135 spectrum all CH-signals occur in the expected region.

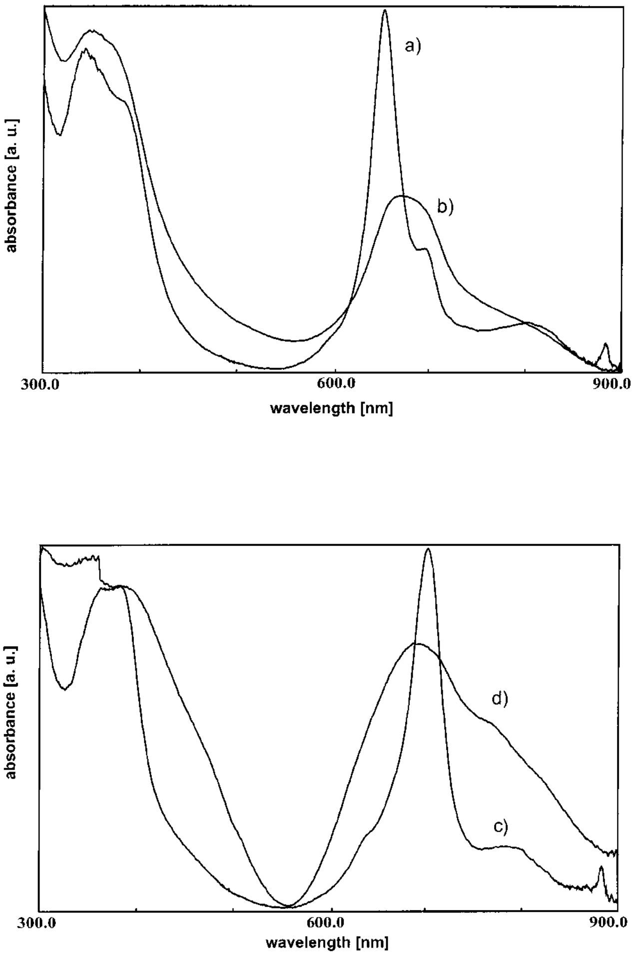


Figure 3. UV/Vis spectra of a) **12** in chloroform b) **12** as a KBr pellet c) **11** in chloroform d) **11** as KBr pellet

Experimental Section

W(NTos)$_2$Cl$_2$,[12] MoNCl$_3$,[7] WNCl$_3$,[7] 4-*tert*-butylphthalonitrile,[18] 4,5-di-*n*-alkylphthalonitriles[19] (alkyl = propyl, butyl, pentyl), nitrido(tetra-*tert*-butyl-phthalocyaninato)rhenium[1,15] and nitrido[octa(*n*-pentyl)phthalocyaninato)rhenium[1] were prepared according to 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, ^{13}C: 62.902, ^{11}B: 80.251 MHz). – Elemental Analyses: Carlo Erba Elemental Analyser 1104, 1106. – EPR: Bruker ESP 300 (X-band).

Nitrido(phthalocyaninato)molybdenum (1): Phthalonitrile (393 mg, 3.08 mmol) was heated with MoNCl$_3$ (147.9 mg, 0.68 mmol) at 220 °C. The temperature was held constant for 20 minutes. After cooling the reaction to room temperature the solid was crushed in a mortar and Soxhlet extracted with acetone and toluene to remove impurities. Yield: PcMoN (**1**) (275 mg, 65%) as a dark green powder. – IR (KBr): $\tilde{\nu}$ = 1605 cm^{-1}, 1549, 1470, 1414, 1331, 1304, 1163, 1119, 1090, 1066, 953 (Mo≡N), 906, 895, 804, 781, 750, 729. – UV/Vis (1-chloronaphthalene): λ = 396.5 nm, 602.5, 639.5, 664.5, 703.5, 777.0. – UV/Vis (KBr): λ = 365.0 nm, 509.5, 609.5, 649.5, 732.0, 791.5. – MS (FAB): *m*/*z* = 623.1 (M$^+$), 514.7 (M$^+$ – MoN). – EPR (1-chloronaphthalene, room temp.): *g* = 1.97.

Nitrido[octa(*n*-alkyl)phthalocyaninato]molybdenum [alkyl = propyl (2), butyl (3), pentyl (4)]: The appropriate 4,5-di-*n*-alkylphthalonitrile (2.08 mmol) was melted with MoNCl$_3$ (100 mg, 0.46 mmol) at 220 °C for 15 minutes. Most of the impurities were removed by column chromatography in the dark on Al$_2$O$_3$ with toluene (two or three times). The solid was then washed several times with methanol. Yield: [(C$_3$H$_7$)$_8$Pc]MoN (**2**) (58 mg, 11%), [(C$_4$H$_9$)$_8$Pc]MoN (**3**) (33 mg, 8%) and [(C$_5$H$_{11}$)$_8$Pc]MoN (**4**) (48 mg, 10%) as green powders.

2: IR (KBr): $\tilde{\nu}$ = 2959 cm^{-1}, 2932, 1618, 1501, 1454, 1402, 1377, 1325, 1261, 1105, 1013, 974 (Mo≡N), 905, 802, 756, 702. – UV/Vis (toluene): λ = 348.5 nm, 647.5, 672.5, 709.0. – MS (FD) (toluene): *m*/*z* = 959.8 (M$^+$). – EPR (toluene, room temp.): *g* = 1.97.

3: IR (KBr): $\tilde{\nu}$ = 3423 cm^{-1}, 3290, 3036, 2957, 2870, 1715, 1643, 1620, 1460, 1377, 1337, 1321, 1211, 1173, 1103, 1013, 962 (Mo≡N), 901, 754, 704. – UV/Vis (toluene): λ = 351.5 nm, 614.5, 647.5, 673.0, 711.5. – MS (FD) (toluene): *m*/*z* = 1072.3 (M$^+$), 962.4 (M$^+$ – MoN). – EPR (toluene, room temp.): *g* = 1.97.

4: IR (KBr): $\tilde{\nu}$ = 2957 cm^{-1}, 2928, 1684, 1645, 1618, 1566, 1520, 1456, 1377, 1330, 1261, 1103, 1015, 974 (Mo≡N), 899, 802, 754, 733. – UV/Vis (toluene): λ = 353.5 nm, 649.5, 679.0, 716.0. – MS (FD) (toluene): *m*/*z* = 1184.8 (M$^+$). – EPR (toluene, room temp.): *g* = 1.97.

Nitrido(phthalocyaninato)tungsten (5): Phthalonitrile (260 mg, 2.04 mmol) was mixed with WNCl$_3$ (138 mg, 0.45 mmol) and melted at 220 °C for 20 minutes. The crude product was then extracted with EtOH, acetone and toluene. Yield: PcWN (**5**) (230 mg, 72%) as a dark green solid. – IR (KBr): $\tilde{\nu}$ = 1604 cm^{-1}, 1470, 1445, 1331, 1308, 1159, 1119, 1064, 953 (W≡N), 895, 812, 783, 750, 729. – UV/Vis (1-chloronaphthalene): λ = 359.5 nm, 673.5, 699.5, 751.0. – UV/Vis (KBr): λ = 355.0 nm, 622.5, 674.5, 704.0, 753.0. – MS (FAB): *m*/*z* = 709.9 (M$^+$). – EPR (solid state, 77 K): *g* = 1.88.

Nitrido[tetra(*tert*-butyl)phthalocyaninato]tungsten (6): A mixture of 4-*tert*-butylphthalonitrile (700 mg, 3.8 mmol) and WNCl$_3$ (255 mg, 0.84 mmol) was heated to 220 °C for 15 minutes. The solid was crushed in a mortar and Soxhlet extracted with hexane to remove the unreacted phthalonitrile. Further impurities were precipitated with CH$_2$Cl$_2$/hexane. The solvent was then removed to give (*t*Bu$_4$Pc)WN (**6**) (110 mg, 14%) as a green solid. – IR (KBr): $\tilde{\nu}$ = 3443 cm^{-1}, 3069, 2963, 2905, 1612, 1516, 1483, 1394, 1366, 1323, 1258, 1200, 1150, 1072, 959 (W≡N), 930, 833, 762, 748. – UV/Vis (toluene): λ = 365.0 nm, 677.0, 745.0. – MS (IS) (MeOH): *m*/*z* = 934.5 (M$^+$). – MS (FAB): *m*/*z* = 934.3 (M$^+$). – EPR (toluene, room temp.): *g* = 1.89.

Nitrido[octa(*n*-pentyl)phthalocyaninato]tungsten (7). Method a): 4,5-Di-*n*-pentylphthalonitrile (500 mg, 1.87 mmol) was melted with WNCl$_3$ (114 mg, 0.37 mmol) at 220 °C for 15 minutes. After extraction of the excess of phthalonitrile with hexane, further impurities were precipitated three times with CH$_2$Cl$_2$/hexane. Removal of the solvent under vacuum gave [(C$_5$H$_{11}$)$_8$Pc]WN (**7**) (43 mg, 9%) as a green solid. **Method b):** 4,5-Di-*n*-pentylphthalonitrile (800 mg, 3.0 mmol) was reacted with W(NTos)$_2$Cl$_2$ (413 mg, 0.66 mmol) at 220 °C for 10 min. The crude product was first washed with three times methanol and further impurities were then precipitated from CH$_2$Cl$_2$/hexane (5×). The solution was separated from solid impurities and the solvent was removed yielding **7** (107 mg, 13%). – IR (KBr): $\tilde{\nu}$ = 3437 cm^{-1}, 3024, 2957, 2928, 2870, 1614, 1483, 1454, 1396, 1325, 1157, 1076, 1011, 957 (W≡N), 893, 814, 746, 733, 685. – UV/Vis (toluene): λ = 376.0 nm, 695.5, 770.5. – MS (FD) (toluene): *m*/*z* = 1270.7 (M$^+$). – EPR (toluene, room temp.): *g* = 1.89.

Oxo[tetra(*tert*-butyl)phthalocyaninato]tungsten (8): (*t*Bu$_4$Pc)WN (31 mg, 0.033 mmol) (**6**) was slowly heated with PPh$_3$ (31 mg, 0.33 mmol) to 250 °C. The temperature was held for 1 h. After cooling to room temperature the solid was chromatographed on Al$_2$O$_3$ (10% H$_2$O) with chloroform as the eluent. The product was then eluted with THF. Finally, further impurities were extracted with hexane to give 15 mg (49%) (*t*Bu$_4$Pc)WO (**8**). – IR (KBr): $\tilde{\nu}$ = 3165 cm^{-1}, 3076, 2963, 2907, 1734, 1722, 1614, 1483, 1464, 1394, 1366, 1327, 1281, 1255, 1200, 1146, 1080, 928, 893, 831, 748, 685, 665. – UV/Vis (toluene): λ = 356.5 nm, 611.0, 674.5, 725.0. – MS (FD) (CH$_2$Cl$_2$): *m*/*z* = 936.5 (M$^+$). – ^{1}H NMR (CDCl$_3$): δ = 1.60–2.26 (36 H, *t*Bu). – ^{13}C NMR (CDCl$_3$): δ = 31.0 (C*C*H$_3$), 32.1 (*C*CH$_3$).

μ-Oxo[oxo{octa(*n*-pentyl)}phthalocyaninato]rhenium (11): (*t*Bu$_4$Pc)-ReN (22.0 mg, 0.0235 mmol) was slowly heated with PPh$_3$ (61.7 mg, 0.235 mmol) to 220 °C at 6×10^{-2} mbar. The temperature was held for 30 minutes. The crude product was then chromatographed on Al$_2$O$_3$ with toluene to remove the impurities. Compound **11** was eluted with CH$_2$Cl$_2$. Yield: [{(C$_5$H$_{11}$)$_8$Pc}Re(O)]$_2$O (**11**) (11 mg, 18%). – IR (KBr): $\tilde{\nu}$ = 2957 cm^{-1}, 2928, 1620, 1485, 1456, 1398, 1377, 1340, 1261, 1138, 1116, 1032, 891, 802, 723, 685, 658. – UV/Vis (CHCl$_3$): λ = 363.5 nm, 380.5, 637.0, 701.5, 778.5. – UV/Vis (KBr): λ = 383.0 nm, 691.0, 768.0, 818.5. – MS (FD) (toluene): *m*/*z* = 2568.2 (M$^+$). – ^{1}H NMR (CDCl$_3$): δ = 1.17–1.23 (t, 24 H, C*H$_3$*), 1.72–1.80 (m, 16 H, CH$_3$C*H$_2$*), 1.91–1.99 (m, 16 H, CH$_3$CH$_2$C*H$_2$*), 2.24–2.30 (m, 16 H, ArCH$_2$C*H$_2$*), 3.41–3.48 (m, 16 H, ArC*H$_2$*), 8.80 (8 H, H-b). – ^{13}C NMR (CDCl$_3$): δ = 14.5 (*C*H$_3$), 23.1 (CH$_3$*C*H$_2$), 32.4 (CH$_3$CH$_2$*C*H$_2$), 32.7 (ArCH$_2$*C*H$_2$), 34.8 (Ar*C*H$_2$), 123.9 (C-b), 135.8 (C-c), 143.4 (C-a), 145.4 (C-d). – ^{13}C NMR (DEPT 135, CDCl$_3$): δ = 14.5 (*C*H$_3$), 23.1 (CH$_3$*C*H$_2$), 32.4 (CH$_3$CH$_2$*C*H$_2$), 32.7 (ArCH$_2$*C*H$_2$), 34.8 (Ar*C*H$_2$), 123.9 (C-b). – C$_{144}$H$_{192}$N$_{16}$O$_3$Re (2567.6): calcd. C 67.36, H 7.54, N 8.73; found C 65.55, H 7.29, N 8.15.

Bis[oxo{tetra(tert-butyl)}phthalocyaninato]rhenium (12): For the synthesis see **11** above. Temperature: 250 °C; reaction time: 45 minutes. Yield: $[(t\mathrm{Bu}_4\mathrm{Pc})\mathrm{Re(O)}]_2$ (**12**) (5 mg, 11%). – IR (KBr): $\tilde{\nu}$ = 2959 cm^{-1}, 2924, 1614, 1485, 1393, 1366, 1335, 1281, 1258, 1198, 1151, 1111, 1092, 1051, 933, 833, 831, 754, 733, 714, 694, 673. – UV/Vis ($\mathrm{CHCl_3}$): λ = 343.0 nm, 380.5, 652.5, 695.0, 801.5. – UV/Vis (KBr): λ = 346.0 nm, 669.5, 774.5. – MS (FD) (toluene): *m*/*z* = 940.2 ($\mathrm{M}^+/2$), 1876.0 ($\mathrm{M}^+ - \mathrm{O}$). – ^{1}H NMR ($\mathrm{CDCl_3}$): δ = 1.70–2.20 (m, 36 H, *t*Bu), 7.70–9.70 (m, 12 H, H-Ar). – $\mathrm{C_{96}H_{96}N_{16}O_3Re_2}$ (1894.3): calcd. C 61.32, H 5.15, N 11.93; found C 58.65, H 4.97, N 11.10.

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