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PAPER

Synthetic, spectroscopic, and structural studies on organoimido molybdenum, tungsten, and rhenium phthalocyanines†

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Unprecedented imido phthalocyaninato complexes of pentavalent refractory metals [PcM(NR)Cl] (M = Mo, W, Re; R = *t*Bu: **1**, **3**, **6**, Mes: **2**, **4**, **7** or Ts: **5**) have been synthesized by reductive cyclotetramerization of phthalonitrile in the presence of appropriate bis(imido) complexes of Mo, W and Re as templates. While d^1 Mo(V) and W(V) species **1–5** show distinctive EPR spectra corresponding to metal centered radicals with hyperfine coupling of two magnetically non-equivalent nitrogen atoms (4 equatorial and 1 axial N), corresponding d^2 Re(V) compounds **6** and **7** are diamagnetic. [PcMo(N*t*Bu)Cl] **1** crystallizes from 1-chloronaphthalene in the tetragonal space group *P*4/*n*. The molecular structure reveals, that the metal center is located above the plane of the equatorial N4 and displaced towards the axial π-donor ligand. Due to the thermodynamic *trans* effect the Mo–Cl bond *trans* to the imido group is elongated to about 2.600(2) Å.

Introduction

As a consequence of their versatility and interesting material properties, metallo phthalocyanines have found a tremendous range of applications in many fields of light-driven processes. Traditionally they serve as thermostable dyes, but during the last decades their functions as photo catalysts, optical limiting materials, photo sensitizers, and molecular semi-conductors, among others, were discovered and refined.[1–4] The chemistry of molybdenum, tungsten, or rhenium accommodated by the phthalocyanine ligand (Pc^{2-}) is so far limited to oxo, halogeno,[5–7] and nitrido complexes.[8] Phthalocyanine complexes incorporating two-valent refractory metals occur as dimers of the type [PcM–MPc] with a molybdenum-molybdenum quadruple or rhenium-rhenium-triple bond, respectively.[7] Hanack *et al.* reported the reaction of nitrido metal phthalocyanines with group 13 Lewis acids EX_3 and trialkyl silyl chloride, leading to PcM≡N → EX_3 adducts and ionic rhenium or neutral tungsten silyl imido compounds.[9] Phthalocyanines of the refractory metals containing organoimido functionalities (PcM═NR) have not been realized so far, even though imido derivatives of Mo, W, and Re supported by other macrocyclic ligands such as porphyrins and calix[4]arenes are known. For example, a Mo(V) imido porphyrin salt [Mo(NMe)(TPP)(H_2O)][I_3] (TPP = tetraphenylporphyrin) was prepared by the reaction of nitrido compound [(TPP)Mo≡N] with methyliodide.[10] Furthermore, Mo(IV) imido porphyrins [(TPP)Mo═NR] (R = aryl) were prepared by reaction of [(TPP)MoCl_2] with 2 equiv. of LiNHR.[11] Other macrocycle-supported imido complexes have been synthesized starting from the preformed imido complexes. For example, organoimido molybdenum and tungsten calix[4]arene (Cax) compounds were prepared by treatment of *p*-*t*Bu-calix[4]arene with [M(N*t*Bu)$_2$(NH*t*Bu)$_2$], with [M(NMes)$_2$Cl$_2$(dme)] (M = Mo or W)[12] and [W(NPh)Cl$_4$],[13] respectively. An imido tungsten calix[4]arene was prepared by the reaction of the disodium salt of a calix[4]arene with [W(NTol)Cl$_4$].[14] Similarly, an imido rhenium calix[4]arene was prepared by the reaction of Cax(OH)$_4$ with [Re(N*t*Bu)$_2$Cl$_3$].[15]

Recently, we reported the synthesis and axial ligand reactivity of soluble, highly reactive imido- and ureato-phthalocyaninato titanium(IV) complexes.[16–17] In this account, we extend these studies to the chemistry of group 6 and 7 metals and describe the synthesis, structural and spectroscopic properties of pure pentavalent molybdenum, tungsten and rhenium complexes of the type [PcM(NR)Cl] **1–7**.

Results and discussion

The organoimido functionality (M = NR; M = Mo, W or Re and R = *t*Bu, Mes or Ts) could be successfully accommodated in the cavity of Pc^{2-} ligand when the cyclotetramerization of phthalonitrile is carried out in the presence of an appropriate metal Lewis acid containing a preformed imido functionality. The Lewis acid does not only act as a precursor for the M═NR group but also as initiator for the cyclotetramerization process, since four molecules of phthalonitrile (PN) do not form phthalocyanines in absence of urea and/or a metal precursor.[1] The use of urea as promoter had to be avoided because the presence of urea promotes

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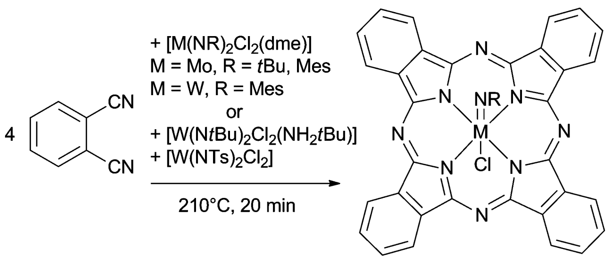
the formation of the metal free PcH_2 rather than the slower process involving the reductive cyclotetramerization of four PN units at the imido metal template. In earlier studies we found, that due to their oxidation potential mono imido precursors $[M(NR)Cl_x]$ lead to aromatic ring-chlorination in the formed Pc's. The discovery of a highly selective synthetic protocol was essential, as PcH_2 or ring-chlorinated Pc's cannot be separated from the desired products.

Imido Mo(V) and imido W(V) phthalocyanines

Melting 4 equiv. of phthalonitrile in the presence of 1 equiv. $[Mo(NR)_2Cl_2(dme)]$[18,19] (R = *t*Bu, Mes), $[W(N\textit{t}Bu)_2Cl_2(NH_2\textit{t}Bu)]$[20] or $[W(NMes)_2Cl_2(dme)]$[19] afford the paramagnetic air stable organoimido compounds [PcM(NR)Cl] **1–4** (Scheme 1). In case of $[W(N\textit{t}Bu)_2Cl_2(NH_2\textit{t}Bu)]$, a low yield of 6% is obtained, in case of $[W(N\textit{t}Bu)_2Cl_2py_2]$ no phthalocyanine was obtained. This is in accord with a mechanism involving Lewis acid induced cyclotetramerization. Phthalodinitrile doesn't replace pyridine. Unfortunately, the ideal precursor for this synthesis $[W(N\textit{t}Bu)_2Cl_2(dme)]$ is not known. Tosylimido phthalocyanine [PcW(NTs)Cl] **5** was obtained by reaction of phthalonitrile with the coordination polymer $[W(NTs)_2Cl_2]$[21] under careful time and temperature control. Hanack *et al.* described the reaction of $[W(NTs)_2Cl_2]$ with substituted phthalodinitriles leading to nitrido phthalocyanines.[9] We believe that the nitrido compounds are formed by TsCl elimination during their work up with protic solvents reported by Hanack *et al.* If extraction of the crude product is solely accomplished with aprotic solvents hydrolytically unstable [PcW(NTs)Cl] **5** and not a hydrolytically rather stable nitrido complex is formed.



M = Mo, R = *t*Bu (**1**), Mes (**2**)
M = W, R = *t*Bu (**3**), Mes (**4**),
Ts (**5**)

Scheme 1 Synthesis of compounds **1–5**.

To provide a plausible mechanism for the formation of these compounds, it is essential to take redox chemistry into account. Two electrons are required for the reduction of four phthalonitrile units to the phthalocyanine dianion (Pc^{2-}). Neither the solvent and reactant PN nor the d^0 metal template can directly provide these electrons. In order to meet the electron balance, formal homolytic cleavage and loss of a nitrene diradical and a chlorine radical at the metal has to be considered during this template reaction at 210 °C. This explains that ring-chlorination can occur as one of the quenching reactions of these radicals. Having a low concentration of chlorine radicals present, this process leads to the selective formation of pure products [PcM(NR)Cl], in which the metal has the oxidation state +V.

The *m*/*z* values of the $[M - Cl]^+$ ions of compounds **1–5** were obtained by MALDI-TOF and APCI-HRMS measurements and show exactly the expected isotopic patterns. The molecular ion peaks (M^+) are much less intense, so that no high resolution spectra could be obtained. They are so low in intensity, that one erroneously might assume from simple standard EI-MS experiments, that the final products have the composition [PcM(NR)]. This shows that the M–Cl bonds are rather weak. To definitely prove that chloride is bound to the central metal and thereby exclude the formation of ring-chlorinated Pc compounds, **1** was reacted with $AgSbF_6$ in a mixture of toluene and THF affording an intensely green suspension and a white precipitate of AgCl. This evidences the presence of inorganic chloride linked to the central metal atom and not to the ring.

$$[PcM(NR)Cl] + AgSbF_6 \rightarrow [PcM(NR)][SbF_6] + AgCl$$

Both APCI and MALDI-TOF spectra of compounds **1–5** do not show the characteristic molecular ion peaks of the analogous nitrido compounds [PcMN], consequently the thermal degradation of the product to the nitrido species can be safely ruled out.

UV-vis spectra of compounds **1–5** show the typical absorption bands of the host macrocycle in the range of 710 nm. Fig. 1 shows the spectra of the tree analogous N*t*Bu compounds **1**, **3** and **6**. A hypsochrome shift of the Q band absorption is observed when going from the Mo compound (718 nm) to W (708 nm) and Re (700 nm). The solubility of compounds [PcM(N*t*Bu)Cl] in 1-chloronaphthalene dramatically decreases in the order M = Mo > W > Re. This might be an indicator for increasing ionic character in the M–Cl bond. Associated with decreasing solubility, additional absorptions at higher wavelength are observed in particular for W and Re derivatives, which is in accord with increasing trend of formation of pairs or higher aggregates. Another explanation for bands at higher wavelengths are metal-to-ligand or ligand-to-metal charge transfer processes.[22]

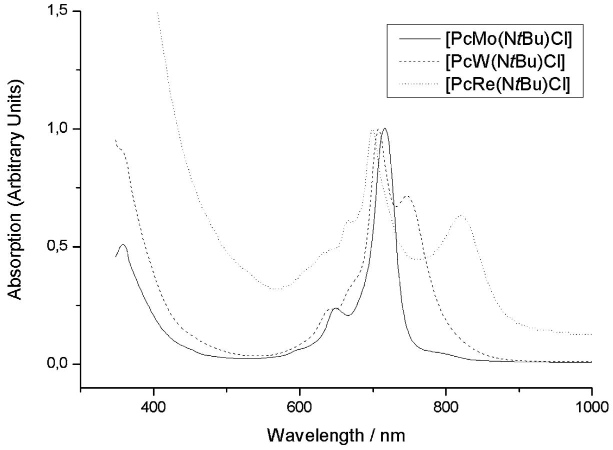


Fig. 1 UV-vis spectra of **1**, **3** and **6** in 1-chloronaphthalene.

IR spectra of compounds **1–5** show the absorptions common for the spectra of the basic Pc moiety (*e.g.* $\nu_{C{=}C\ arom.}$ at nearly 1602 cm^{-1}). Compared to the IR spectra of PcH_2[1] and [PcTi(NR)],[16,23] new absorptions were observed in the spectra of **1** and **2** such as the shoulder at about 1260 cm^{-1}, which can be assigned to $\nu_{Mo{=}N}$ in the Mo=N–C system. Additionally, IR

Table 1 *g* values of **1**, **2** and selected Mo(V) compounds

	g	Ref.
[PcMo(N*t*Bu)Cl] (**1**)	1.979	This work
[PcMo(NMes)Cl] (**2**)	1.972	This work
[PcMoN]	1.97	9
[TPPMo(NMe)(H_2O)][I_3]	1.9766	10
[TTPMoOCl]	1.971	25

spectra of **1** and **2** did not evidence the characteristic Mo≡N stretching band at 953 cm^{-1}, which was present for [PcMo≡N].[8,9] Similarly, the IR spectra of **3**, **4** and **5** did not evidence the characteristic (W≡N) stretching band at 959 cm^{-1}, which was present for [PcW≡N].[8,9] Raman spectra of **1** and **2** both show the skeletal vibrations in the frequency range 1300–1610 cm^{-1} and in the high frequency region. The spectra were obtained by excitation at 432 nm. An important feature in the Raman spectra of **1** and **2** is the absence of the characteristic absorption of $\nu_{\text{Mo–Mo}}$ around 310 cm^{-1} and consequently the formation of a d^1–d^1 M–M bonded molybdenum phthalocyanine dimer can be safely ruled out.[24] Similarly, in the Raman spectra of **3** and **4**, the absorption of a W–W bond at about 275 cm^{-1} is absent.[24]

EPR spectra of imido Mo(V) and imido W(V) phthalocyanines 1–5

EPR spectra of solutions of **1–5** in toluene/1-chloronaphthalene (3 : 1) were recorded at various temperatures and are consistent with the expected values for d^1 molybdenum compounds. The experimental and simulated spectra of **1** are shown in Fig. 2. The super hyperfine structure is in accordance with the simulation for the coupling of the central metal with two kinds of non-equivalent nitrogen atoms N_{ax} and N_{eq} (Fig. 2). The g values of 1.979 for **1** and 1.972 for **2**, respectively, are comparable with those found for other porphyrinoid Mo(V) compounds (Table 1). Similarly, the experimental epr spectra of W(V) compounds **3** and **4** are in accordance with the simulations. The g_{iso} values are 1.959 for **3**, 1.914 for **4** and 1.88 **5** (solid state), respectively. This supports the suggested structure, in which the metal is surrounded by the macrocycle occupying the four equatorial positions and the imido and chloride ligands in the axial positions.

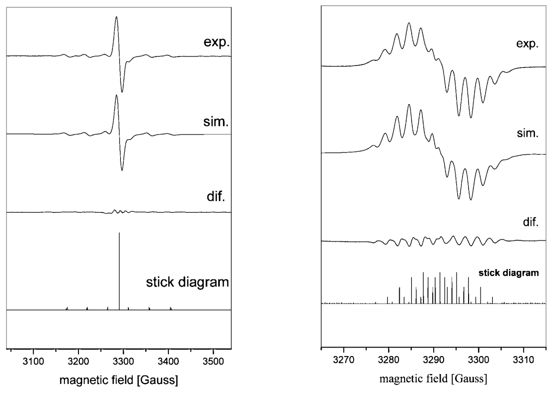


Fig. 2 Left: the hyperfine structure of molybdenum in the EPR spectrum of **1** (toluene/1-chloronaphthalene, 330 K). Right: the super-hyperfine structure of molybdenum and 5 N atoms (4 N_{eq} are equal) in **1** and the stick diagram (220 K, modulation amplitude 1 Gpr).

Table 2 Selected bond distances (Å) and angles (°) of **1**

Mo1–N11	1.704(7)	Cl1–Mo1–N11	180
Mo1–N1	2.054(3)	Mo1–N11–C10	162.9(7)
Mo1–Cl1	2.600(2)	N1–Mo1–N1a	88.73(3)
N11–C10	1.424(15)		

Crystal structure of [PcMo(N*t*Bu)Cl] 1

Crystallization of **1** from non-dried 1-chloronaphthalene as obtained from Acros did not lead to hydrolysis of the compound but to formation of a crystalline hydrate. This stability against hydrolysis is characteristic for d^1 Mo organoimido complexes rather than for d^0 complexes. The molecular structure of **1** in the solid state is shown in Fig. 3. Selected bond distances and angles of **1** are given in Table 2.

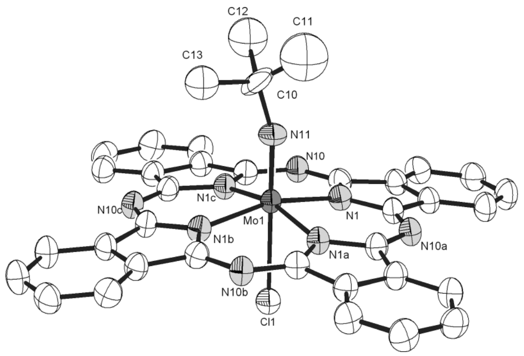


Fig. 3 Molecular structure of **1**. Displacement ellipsoids are shown at the 50% probability level. (H atoms and disordered positions of the *tert*-butyl group due to fourfold crystallographic symmetry are omitted for clarity. Letters a, b and c indicate the following symmetry operations: a = 1/2 − *y*, *x*, *z*; b = 1/2 − *x*, 1/2 − *y*, *z*; c = *y*, 1/2 − *x*, *z*.)

Seven disordered molecules of water per molecule of **1** are observed and omitted for clarity. The molybdenum atom is octahedrally coordinated by the four isoindoline nitrogen atoms (N_{eq}) forming the basal plane and two axial ligands, the imido group and the chlorine atom. **1** exhibits fourfold crystallographic rotational symmetry with Mo, Cl, and N11 lying on the fourfold rotation axis. As a consequence, the *tert*-butyl group's atomic positions deviating from this axis are disordered in four crystallographically imposed positions. The distances Mo–N_{eq} = 2.054(3) Å as well as angles N1–Mo–N1b = N1a–Mo–N1c = 162.90(19)° are equal due to this symmetry. Both values are comparable to those reported for porphyrin complex [Mo(NMe)(TPP)(H_2O)][I_3]; 2.097(6) Å and 162.58(25)°, respectively.[10] The four equal angles N_{eq}–Mo–N_{ax} of 98.55(9) Å compare well with an average N_{eq}–Mo–N_{ax} of 99.1° reported for [Mo(NMe)(TPP)(H_2O)][I_3]. The strong thermodynamic *trans* effect of the imido ligand in combination with steric repulsion between the *tert*-butyl group and the four N_{eq} atoms in **1** induces a displacement of the molybdenum atom towards the imido N atom, thereby creating a shallow dome with the four N_{eq} atoms.[10,26] The molybdenum atom lies 0.305 Å above the plane defined by the four N_{eq} atoms, which is comparable to 0.334 Å in [Mo(NMe)(TPP)(H_2O)][I_3], but less than in pentacoordinate [PcMoO] (0.69 Å)[5] and [(TTP)Mo=S] (0.65 Å).[27] The Mo=N distance of 1.704(7) Å observed for **1** compares well with that of 1.689(6) Å in [Mo(NMe)(TPP)(H_2O)][I_3]. The angle C10–N11–Mo of 162.9(7)° in **1** deviates stronger from linearity than 175.34(64)° reported for [Mo(NMe)(TPP)(H_2O)][I_3]. An angle of 160–180° is common for many other organoimido complexes. The Mo–Cl distance of 2.600(2) Å observed for **1** is elongated compared to those of 2.347(4) and 2.276(4) Å reported for [(TTP)$MoCl_2$].[28] This distance suggests a weak interaction and a higher ionic character of the M–Cl bond compared to porphyrinoid complexes without axial π-donor ligands.

Molecular packing of 1

Fig. 4 shows the molecular packing of [PcMo(N*t*Bu)Cl] **1** in the unit cell. The presence of two axial substituents (Cl and N*t*Bu) results in a reduction of the degree of π-stacking compared to four and five-coordinate metallo Pc's.

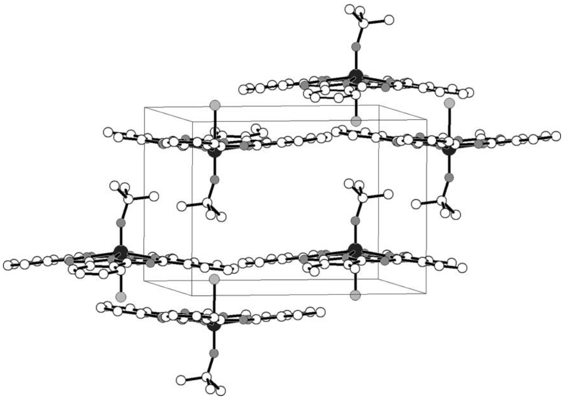


Fig. 4 View of the molecular packing of **1** along the Pc planes. H atoms, disorder of the N*t*Bu group and solvent molecules are omitted for clarity.

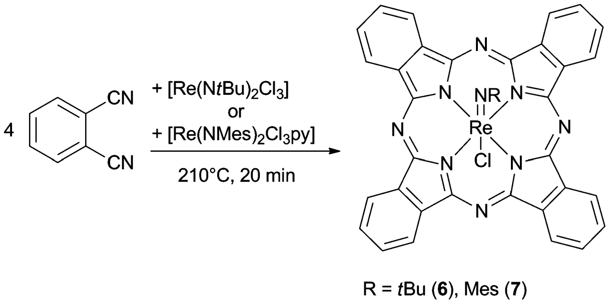
Due to the molecular shape the crystal does not contain close packed face-to-face dimers, which is commonly observed for metal phthalocyanines containing only one axial ligand (*e.g.* [PcMoO],[5] [PcTi(NDip)][16]). A layered structure of essentially co-planar Pc-rings is observed. Regarding the planes defined by the N_{eq} atoms, alternating short (d = 4.031 Å) and long (6.062 Å) interlayer distances are observed, reflecting the different steric demand of the layer separating chlorine atoms and water molecules *vs.* the bulkier *tert*-butyl imido groups, respectively. Therefore, the molecules are much less densely packed in crystalline **1** compared to [PcMoO] and [PcTi(NDip)]. The interaction between the macrocycles' π-systems is greatly reduced, which enhances the solubility in rather polar organic solvents such as chloronaphthalene and THF. A comparison of selected distances is given in Table 3.

Imido Re(V) phthalocyanines

Fusion of phthalonitrile in the presence of [Re(N*t*Bu)$_2$$Cl_3$][29] or [Re(NMes)$_2$$Cl_3$py][29] (210 °C, 20 min) affords the diamagnetic imido phthalocyaninato rhenium(V) complexes [PcRe(NR)Cl] (R = *t*Bu **6** or Mes **7**) (Scheme 2).

Table 3 Selected intermolecular distances (Å) in [PcMX] (interlayer distance = shortest distance between neighbouring N_{eq} planes)

	1	[PcMoO]	[PcTi(NDip)]
Shortest distance M–M	10.815 (sep. by Cl) 11.187 (sep. by N*t*Bu)	7.3587	4.7709
Interlayer distance	4.031 (sep. by Cl) 6.062 (sep. by N*t*Bu)	3.5186	3.4084



Scheme 2 Synthesis of compounds **6** and **7**.

^{1}H-NMR spectra of **6** and **7** could be obtained in C_6D_5Br at 100 °C, although the intensity of the signals is poor due to the solubility. The spectra of **6** and **7** show two multiplets in the aromatic region, the first multiplet in the region 9.7 ppm for the eight protons in the 1,4-positions and the second multiplet in the region 8.3 ppm for the eight protons in the 2,3-positions. As a result of the well known ring current effect in phthalocyanines,[30,31] the aliphatic protons show a drastic upfield-shift (*tert*-butyl group in **6** at −1.52 ppm and methyl groups in **7** at −0.51 and 1.12 ppm). Similarly, the aromatic protons of the axial ligand of **7** exhibit an expected upfield shift as they are found in the region of 5.66 ppm. No single crystals of **6** and **7** suitable for X-ray crystallography could be obtained, but an analogous structure to **1** can be tentatively assumed. The *m/z* values for the [M^+ – Cl] ions of the prepared complexes [PcRe(NR)Cl] **6** and **7** were obtained with the expected isotopic patterns in both APCI and MALDI-TOF measurements. The low values of %C in the elemental analyses obtained for **6** and **7** are attributed to the formation of the thermally extremely stable rhenium carbides at elevated temperatures. Chlorine analysis confirms the monochloro rhenium complex. UV-vis spectra of both **6** (Fig. 1) and **7** in chloronaphthalene display the common Q-band maxima in the expected region.[8,9] Compared to the IR spectra of [PcR_nReO][8] and [PcR_nReN] (R = alkyl),[8,9] the medium-strong band at 1288 cm^{-1} observed in IR spectra of **6** and **7** can be assigned to the Re═N–C stretching. The IR spectra of **6** and **7** do not show the characteristic Re≡N stretching band at 953 cm^{-1} present in [PcRe≡N].[8,32]

Conclusions

In an extension of our previous work on the synthesis of imido titanium phthalocyanines, we herein reported a convenient synthetic protocol for the first organoimido metal phthalocyanines of group 6 and 7 [PcM(NR)Cl] (M = Mo, W, Re). Loss of an imido group [NR]$^{2-}$ as nitrene [NR] diradical at an imido metal template seems to be the key to a more general strategy towards the synthesis of interesting axially functionalized metallo phthalocyanines. The result of this multi-step reaction in molten phthalodinitrile is the formal substitution of [NR]$^{2-}$ by [Pc]$^{2-}$.

Experimental

All experiments and manipulations were carried out under dry nitrogen or argon atmosphere using standard Schlenk or glove-box techniques. Solvents—if not stated otherwise—were rigorously purified with appropriate drying agents, distilled and stored over molecular sieves under nitrogen. Chloronaphthalene was purchased from Acros as a mixture of 90% of 1-chloronaphthalene and 10% of 2-chloronaphthalene. Phthalonitrile was sublimed under reduced pressure prior to use. The electronic spectra were recorded on a Shimadzu UV-1601 PC-spectrophotometer. IR spectra were recorded on a Bruker IFS 588 spectrometer. APCI mass spectra were taken on a Finnigan LTQ-FT Spectrometer using methanol as solvent. MALDI–TOF mass spectra were taken on a Bruker Biflex III using pyrene as matrix. Elemental analysis of C, H and N elements was carried out using an Elementar, Vario EL. ^{1}H-NMR spectra of the phthalocyanines were recorded on a Bruker AMX 500.

[Mo(N*t*Bu)$_2$Cl$_2$(dme)][18] [Mo(NMes)$_2$Cl$_2$(dme)],[19] [W(N*t*Bu)$_2$-Cl$_2$(H$_2$N*t*Bu)],[20] [W(NMes)$_2$Cl$_2$(dme)],[19] [W(NTs)$_2$Cl$_2$],[21] [Re(N*t*-Bu)$_2$Cl$_3$][29] and [Re(NMes)$_2$Cl$_3$py][29] were prepared according to literature procedures.

General Procedure for the Preparation of 1–7

A mixture of 4.4 equiv. phthalonitrile and 1 equiv. of the respective bis(imido) precursor (**1**: [Mo(N*t*Bu)$_2$Cl$_2$(dme)], **2**: [Mo(NMes)$_2$Cl$_2$(dme)], **3**: [W(N*t*Bu)$_2$Cl$_2$(NH$_2$N*t*Bu)], **4**: [W(NMes)$_2$Cl$_2$(dme)], **5**: [W(NTs)$_2$Cl$_2$], **6**: [Re(N*t*Bu)$_2$Cl$_3$], **7**: [Re(NMes)$_2$Cl$_3$py]) was finely ground in a mortar under nitrogen until a homogeneous powder was obtained. The mixture was quickly heated at melt at 210 °C for 20 min by using a preheated metal bath of Wood alloy. The produced dark-green solid was suspended in 50 mL of toluene and the suspension was treated with ultrasound at 70 °C for 2 h. The precipitate was collected on a glass frit and purified by successive extractions with refluxing toluene (10 × 50 mL), MeCN (10 × 50 mL) and finally washed with pentane. The black-green solid was dried at 140 °C and 10^{-5} mbar for 5 h.

[PcMo(N*t*Bu)Cl] 1. 282 mg phthalonitrile (22 mmol) and 200 mg [Mo(N*t*Bu)$_2$Cl$_2$(dme)] (5 mmol). Yield: 220 mg (67%). Anal. calcd for $C_{36}H_{25}ClMoN_9$: C 60.47, H 3.52, N 17.63. Found: C 59.61, H 4.33, N 17.12. UV-vis λ_{max}/nm (1-chloronaphthalene): 718 (s), 648 (sh), 358 (s). ν_{max}(KBr)/cm^{-1}: 1602 (m), 1463 (m), 1328 (s), 1284 (w), 1265 (m) 1161 (w), 1115 (s), 1063 (m), 973 (w), 893 (m), 802 (w), 772 (w), 750 (m), 728 (s), 570 (w). EPR (1-chloronaphthalene/toluene 1 : 3, 130 K): $g_1 = 1.989$, $g_2 = 1.987$, $g_3 = 1.977$. MALDI-TOF-MS (*m*/*z*) 716.2 [M$^+$], 681.3 [M$^+$ – Cl], APCI-HRMS (*m*/*z*) 681.1289 [M$^+$ – Cl], $C_{36}H_{25}N_9Mo$ requires 681.1282.

[PcMo(NMes)Cl] 2. 282 mg phthalonitrile (22 mmol) and 262 mg [Mo(NMes)$_2$Cl$_2$(dme)] (5 mmol). Yield: 280 mg (72%). Anal. calcd for $C_{36}H_{25}ClMoN_9$: C 63.36, H 3.50, N 16.22, Cl 4.6. Found: C 63.84, H 3.76, N 14.55, Cl 5.8. UV-vis λ_{max}/nm (1-chloronaphthalene): 732 (s), 668 (sh), 364 (s). IR ν_{max}(KBr)/cm^{-1}: 1602 (m), 1462 (m), 1327 (s), 1286 (w), 1260(Mo=N–C), 1161 (w), 1114 (s), 1063 (w), 972 (m), 891 (m), 802 (w), 772 (w), 749 (m), 727 (s), 569 (w). EPR (1-chloronaphthalene/toluene 1 : 3, 130 K): $g_1 = 1.986$, $g_2 = 1.981$, $g_3 = 1.974$. MALDI-TOF-MS (*m*/*z*) 778 [M$^+$], 743 [M$^+$ – Cl]. APCI-HRMS (*m*/*z*) 743.1439 [M$^+$ – Cl], $C_{41}H_{27}N_9Mo$ requires 743.1438.

[PcW(N*t*Bu)Cl] 3. 400 mg phthalonitrile (3.13 mmol) and 367 mg [W(N*t*Bu)$_2$Cl$_2$(NH$_2$*t*Bu)] (0.78 mmol). Yield: 35 mg, (6%). Anal. calcd for $C_{36}H_{25}ClN_9W$: C 53.85, H 3.14, N 15.70, Cl 4.41. Found: C 51.33, H 4.01, N 15.40, Cl 5.15. UV-vis λ_{max}/nm (1-chloronaphthalene): 746 (sh), 708 (s), 348 (s). IR ν_{max}(KBr)/cm^{-1}: 2994 (s, ν(CH$_{aliph.}$)), 1604 (w), 1467 (m), 1408 (w), 1332 (s), 1286 (m), 1162 (w), 1115 (s), 966 (s), 956 (w), 891 (m), 853 (w), 773 (m), 750 (m), 724 (s), 571 (w). EPR (1-chloronaphthalene/toluene 1 : 3, 293 K): $g_{iso} = 1.959$. MALDI-TOF-MS (*m*/*z*) 802.4 [M$^+$], 767.4 [M$^+$ – Cl]. APCI-HRMS (*m*/*z*) 767.1750 [M$^+$ – Cl], $C_{36}H_{25}N_9W$ requires 767.1737.

[PcW(NMes)Cl] 4. 520 mg phthalonitrile (4.06 mmol) and 577 mg [W(NMes)$_2$Cl$_2$(dme)] (0.94 mmol). Yield: 580 mg (71%). Anal. calcd for $C_{41}H_{27}ClN_9W$: C 56.93, H 3.14, N 14.57, Cl 4.1. Found: C 56.17, H 3.15, N 13.90, Cl 5.01. UV-vis λ_{max}/nm (1-chloronaphthalene): 870.0 (m), 731.0 (s), 664.0 (m). IR ν_{max}(KBr)/cm^{-1}: 1605 (w), 1468 (m), 1404 (w), 1329 (s), 1284 (m), 1161 (w), 1117 (s), 966 (s), 951 (w), 893 (m), 853 (w), 773 (m), 749 (m), 724 (s), 571 (w). EPR (1-chloronaphthalene/toluene 1 : 3, 130 K): $g_1 = 1.927$, $g_2 = 1.908$, $g_3 = 1.911$. MALDI-TOF-MS (*m*/*z*) 864.4 [M$^+$], 829.4 [M$^+$ – Cl]. APCI-HRMS (*m*/*z*) 829.1902 [M$^+$ – Cl], $C_{41}H_{27}N_9W$ requires 829.1983.

[PcW(NTs)Cl] 5. 200 mg phthalonitrile (1.56 mmol) and 136 mg [W(NTs)$_2$Cl$_2$] (0.35 mmol). Yield: 137 mg (45%). Anal. calcd for $C_{39}H_{23}ClN_9O_2SW$: C 51.99, H 2.57, N 13.99. Found: C 51.26, H 2.91, N 13.33. UV-vis λ_{max}/nm (1-chloronaphthalene): 762 (s), 385 (s). IR ν_{max}(KBr)/cm^{-1}: 2915 (w), 1619 (m), 1601 (w), 1519 (w), 1464 (s), 1326 (s), 1287 (s), 1154 (m), 1117 (m), 1057 (s), 892 (w), 768 (m), 725 (s), 552 (m). EPR (solid state, 8 K): $g_1 = 1.88$. APCI-HRMS (*m*/*z*) 865.1207 [M$^+$ – Cl], $C_{39}H_{23}N_9O_2SW$ requires 865.1203.

[PcRe(N*t*Bu)Cl] 6. 400 mg phthalonitrile (3.12 mmol) and 308 mg [Re(N*t*Bu)$_2$Cl$_3$] (0.71 mmol). Yield: 260 mg (42%). Anal. calcd for $C_{36}H_{25}N_9ClRe$: C 53.69, H 3.13, N 15.65, Cl 4.4. Found: C 51.84, H 2.70, N 17.25, Cl 4.7. (Despite the diligent purification of the product and multiple attempts, no better elemental analysis could be obtained). UV-vis λ_{max}/nm (1-chloronaphthalene): 820 (sh), 700 (s), 341.0 (w), 323.0 (s). IR ν_{max}(KBr)/cm^{-1}: 2969 (w), 1771 (w), 1717 (w), 1652 (w), 1609 (w), 1558 (w), 1522 (w), 1473 (s), 1409 (w), 1361 (w), 1334 (s), 1287 (m), 1260 (Re=N–C), 1184 (w), 1167 (w), 1119 (m), 1101 (m), 1064 (w), 902 (w), 776 (w), 755 (w), 732 (s). ^{1}H-NMR (500 MHz, C_6D_5Br, 373 K) δ (ppm): –1.55 (s, 9 H, CMe$_3$), 8.34–8.47 (m, 8 H, 2,3-Pc), 9.81–9.86 (m, 8 H, 1,4-Pc). APCI-MS (*m*/*z*) 804 [M$^+$], 769 [M$^+$ – C1], MALDI-TOF-MS (*m*/*z*) 805.5 [M$^+$], 770.3 [M$^+$ – Cl].

[PcRe(NMes)Cl] 7. 898 mg phthalonitrile (7.02 mmol) and 1.02 g [Re(NMes)$_2$Cl$_3$py] (1.60 mmol). Yield: 1.15 g, (83%). Anal. calcd for $C_{41}H_{27}N_9ClRe$ C 56.77, H 3.14, N 14.53, Cl 4.08. Found: C 52.17, H 2.39, N 15.24, Cl 3.80 (Despite the diligent purification of the product and multiple attempts, no better elemental analysis could be obtained). UV-vis λ_{max}(1-chloronaphthalene)/nm 736 (s), 664 (sh), 364 (s), 321.4 (s); IR ν_{max}(KBr)/cm^{-1} 1607 (w), 1474 (m), 1410 (w), 1331 (s), 1287 (w), 1261 (Re=N–C) 1167 (m), 1119 (m), 1100 (w), 1063 (w), 901 (m), 872 (w), 807 (w), 775 (m), 754 (m), 727 (s); ^{1}H-NMR (500 MHz, C_6D_5Br, 373 K) δ (ppm) –0.51 (s, 6 H, *o*Me), 1.12 (s, 3 H, *p*Me), 5.56 (s, 2 H, Mes), 8.26–8.45 (m, 8 H,

Table 4 X-Ray data collection parameters of **1**

Compound	**1**
Empirical formula	$C_{36}H_{39}ClMoN_9O_7$
Formula weight	841.15
Crystal system	Tetragonal
Space group	$P4/n$
a/Å	13.8148(12)
b/Å	13.8148(12)
c/Å	10.0926(9)
V/Å^3	1926.2(3)
Z	2
ρ_{calcd}/Mg m^{-3}	1.450
μ/mm^{-1}	0.469
Reflections collected	12 104
Independent reflections	1702
R_{int}	0.0865
Reflections with $I > 2\sigma(I)$	1424
Goodness-of-fit on F^2	1.100
R_1 (observed data)	0.0497
wR_2 (all data)	0.0978

2,3-Pc), 9.64–9.85 (m, 8 H, 1,4-Pc); APCI-MS (m/z) 832 [M$^+$ – Cl], MALDI-TOF-MS (m/z) 868.0 [M$^+$], 832.8 [M$^+$ – Cl].

X-Ray crystallography

Selected crystallographic data of **1** are given in Table 4. The complete data are given in the CIF file (ESI).† Data were collected on a Stoe IPDS-II area detector system using a graphite monochromated Mo-Kα X-radiation (λ = 0.71073 Å). The structure was solved by direct methods (program SIR2002[33]) and refined on F^2 by full matrix least squares using SHELXL-97.[34] All non hydrogen atoms were refined as anisotropic, the hydrogen atom positions were calculated and refined using the 'riding model' with fixed isotropic thermal parameters. There is a fourfold crystallographic disorder of the N-*t*-butyl group. Disordered solvent has been refined introducing O-atoms of disordered water molecules.

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