Studies on Phosphorus Phthalocyanines and Triazatetrabenzcorroles

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The previously reported reaction of phthalocyanines [H_2(pc)] with PBr_3, which was claimed to give a phosphorus(III) phthalocyanine "(PcP^{III})", has been reinvestigated in detail with both unsubstituted and alkyl-substituted phthalocyanines, **1–4**. The products exhibit unusual electronic and mass spectra compared to normal phthalocyanines and have been identified as oxophosphorus(V) triazatetrabenzcorroles **5–8**. The corresponding dihydroxyphosphorus(V) phthalocyanine hydroxides **9–12** have also been synthesized for the first time by insertion of phosphorus(V) into phthalocyanines and have been characterized in detail. The different reactivities of PBr_3 and POX_3 (X = Cl, Br) toward phthalocyanines are discussed.

Introduction

Metal phthalocyanines, the most extensively studied macrocyclic compounds in dyestuff and coordination chemistry,[1] are currently of great interest owing to their potential technical applications in a variety of new fields such as liquid crystals, molecular metals, chemical sensors, electrocatalysis, and in photodynamic cancer therapy.[2] As a result, several metal phthalocyanines bearing different substituents either on the periphery or at the axial position of the macrocycles have been synthesized and characterized. Phthalocyanines containing metalloids and non-metals of groups 14 and 15[1][3] are of particular chemical and spectroscopic interest because two different oxidation states are accessible for the central atom. However, in contrast to porphyrin complexes of group-14 and -15 elements (phosphorus,[4] arsenic,[5] antimony,[6] and bismuth[7]), which have been extensively investigated, there have only been a few reports on studies of the phthalocyanine complexes of these elements.[8] Among these, antimony and bismuth phthalocyanines are available with the two oxidation states Sb^{III} and Sb^{V}[8c] and Bi^{II} and Bi^{III},[8b][9] respectively. In the case of arsenic, only chloroarsenic phthalocyanine has been reported and characterized by UV/Vis spectroscopy, which displays a blue-shifted (λ_{max} = 580 nm) absorption of the Q band compared with other metal phthalocyanines.[8a]

In 1981, Gouterman and co-workers first reported the synthesis of the so-called "PcP^{III}" and "PcP^{V}" species.[10] The authors pointed out that the "PcP^{III}" obtained showed a sharp Soret band at 422 nm in its UV/Vis spectrum, in contrast to the broad Soret band at ca. 330 nm observed for phthalocyanines in general. Furthermore, the "PcP^{III}" thus obtained exhibited an unusual mass spectrum corresponding to [PH_2(pc)]$^+$. Later, in their review[7] on the preparation and electronic spectra of metalloid porphyrins and phthalocyanines, the same authors pointed out that the soluble "[P^{III}(*t*Bu$_4$pc)]$^+$" species obtained also display the same unusual electronic and mass spectra as those found for [PH_2(*t*Bu$_4$pc)]$^+$. However, several questions concerning the structures of phosphorus(III) phthalocyanines still needed to be clarified.[7]

Recently, during our studies on the synthesis of precursors for polymers containing phthalocyanine units, 4,5-dipentyldiiminoisoindoline was treated with Si_2Cl_6 in order to examine the potential of producing phthalocyanine dimers containing an Si−Si bond.[11] Unexpectedly, the substituted hydroxysilicon triazatetrabenzcorrole Si(OH)[(C_5H_{11})$_8$tbc], a phthalocyanine-like macrocycle that was first characterized by Fujiki et al.,[12] was obtained. We noticed that the UV/Vis spectrum of Si(OH)[(C_5H_{11})$_8$tbc] prepared as above was very similar to those of the supposed phosphorus(III) phthalocyanines reported by Gouterman et al.[10]

A literature search revealed that Liu et al.[13] had carried out the reaction of PBr_3 with the metal-free tetrasubstituted phthalocyanine, H_2[(OPr)$_4$pc] in pyridine, following the literature procedure reported for the unsubstituted metal-free phthalocyanine[10]. The product obtained was, however, believed to be the hydrogen hydroxyphosphorus(III) tetraisopropyloxytriazatetrabenzcorrole {PH[(OPr)$_4$tbc](OH)}. The earlier product obtained from the unsubstituted phthalocyanine was therefore postulated to have the structure [PH(tbc)](OH).[10] While the UV/Vis spectrum of the reported "PcP^{III}" resembled that of the triazatetrabenzcorrole derivative that we had prepared,[11] on repeating the reaction of metal-free phthalocyanines with PBr_3 we found the mass-spectral pattern of the product obtained to be completely different from the data assigned to the formula [PH(tbc)](OH).[13] This discrepancy prompted us to rein-

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vestigate the structure of the phosphorus(III) phthalocyanine species reported in the original work.[10] We have carried out reactions of unsubstituted H_2(pc) and of the alkyl-substituted phthalocyanines **2**−**4** with the trivalent phosphorus reagent PBr_3. All the complexes obtained were found to exhibit the similar distinctive UV/Vis and mass spectra as those of the phosphorus(III) phthalocyanine species "PcP^{III}" reported by Gouterman et al.[10] We present here our results based on spectroscopic measurements and show that these complexes are in fact oxophosphorus(V) triazatetrabenzcorroles, which arise from a ring-contraction reaction of phthalocyanines. In addition, we have also carried out the reactions of substituted and unsubstituted phthalocyanines with $POBr_3$ and $POCl_3$ for the first time and have identified the products as [P(OH)$_2$(R_8pc)](OH).

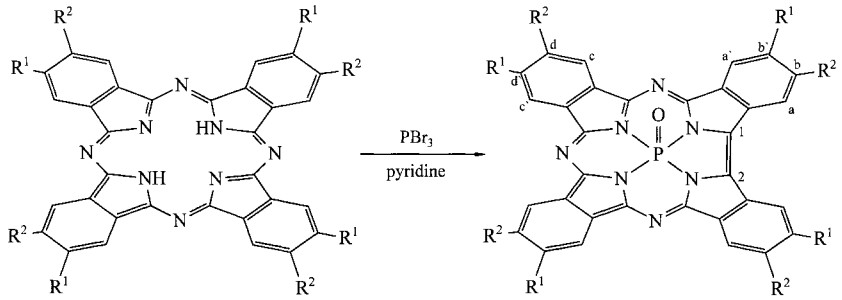
Results and Discussion

The reaction of PBr_3 with the metal-free phthalocyanines **1**−**4** in pyridine, following the literature procedure,[10] afforded the oxophosphorus(V) triazatetrabenzcorrole complexes **5**−**8** in moderate yields (Scheme 1). The products obtained were purified by column chromatography. Figure 1 shows the UV/Vis spectrum of complex **5** in pyridine, which is almost identical to that reported[10] for "PcP^{III}" in pyridine/CH_2Cl_2 (1:20). The very unusual spectrum, with a sharp Soret band at 442 nm of an intensity almost twice that of the Q band, was attributed to the porphyrin-like four-orbital electronic transitions $a_{1u}(\pi)$, $a_{2u}(3p_z) \rightarrow e_g(\pi^*)$, where $a_{1u}(\pi)$ and $a_{2u}(\pi)$ are nearly degenerate[10]. The UV/Vis-spectral characterization of "PcP^{III}" was based on the fact that its spectrum in neat trifluoroacetic acid (TFA) was identical to spectra obtained for either H_2(pc) or Li_2(pc) in neat TFA, although the spectrum was not reproduced in the paper.[10] In Figure 1, the UV/Vis spectra of **5** in pyridine and TFA are compared. The other tbc complexes **6**−**8** that we have prepared show similar spectral patterns in TFA. The absorption of complex **5** in TFA shows a red shift compared to that in pyridine and appears as several structureless broad bands without splitting. In fact, when the TFA solution of complex **5** was diluted with water, **5** could be recovered without any detectable change in its UV/Vis spectrum. Even after 12 h reflux in TFA under nitrogen and protected from light, the UV/Vis spectrum did not change, highlighting the unique stability of **5** towards acid. A similar phenomenon was also observed in the case of SiOH[$(C_5H_{11})_8$tbc], as we reported recently.[11] We treated the complex with concentrated H_2SO_4, H_3PO_4, H_3PO_4 + CH_3CO_2H, and TFA in the hope of obtaining the metal-free tbc macrocycle, but only unreacted SiOH[$(C_5H_{11})_8$tbc] could be recovered.

The FAB-MS spectrum of complex **5** shows a peak at m/z = 545.2, which is in good agreement with both the value observed by Gouterman et al.[10] for the complex "PcP^{III}" (545.4) and the theoretical value for complex **5** (545.1). Evidently, oxygen (m/z = 16) was mistaken for NH_2 (m/z = 16). Compounds **6**, **7** and **8** prepared according to Scheme 1 display the same type of mass spectra and give the expected fragments. Among these, complex **6** shows the same molecular ion peak as that of $[P^{III}(t\text{Bu}_4\text{pc})H_2]^+$, later reported by Gouterman et al. in their review.[7]

Liu et al.[13] have also repeated the work of Gouterman using a substituted phthalocyanine and obtained a complex the structure of which was shown to be {HP[$(OPr)_4$-tbc]}(OH). They postulated that the structure of "PcP^{III}"[10] should be [HP(tbc)](OH). However, we have not been able to observe the mass peak for $[M - H]^+$, nor that for $[M^+]$, corresponding to the formula [HP(tbc)](OH) in the mass spectrum of **5**, despite the fact that these are reported to be two of the most intense peaks in the mass spectrum of {HP[$(OPr)_4$tbc]}(OH). Moreover, none of the other phosphorus tbc complexes that we have prepared show mass peaks for $[M - H]^+$ or $[M^+]$ expected for the formula [HP(R_8tbc)](OH) in their respective mass spectra either. On the basis of these results, it would appear that the formula [HP(R_8tbc)](OH) is not the correct one for the phosphorus tbc complexes as reported.[13]

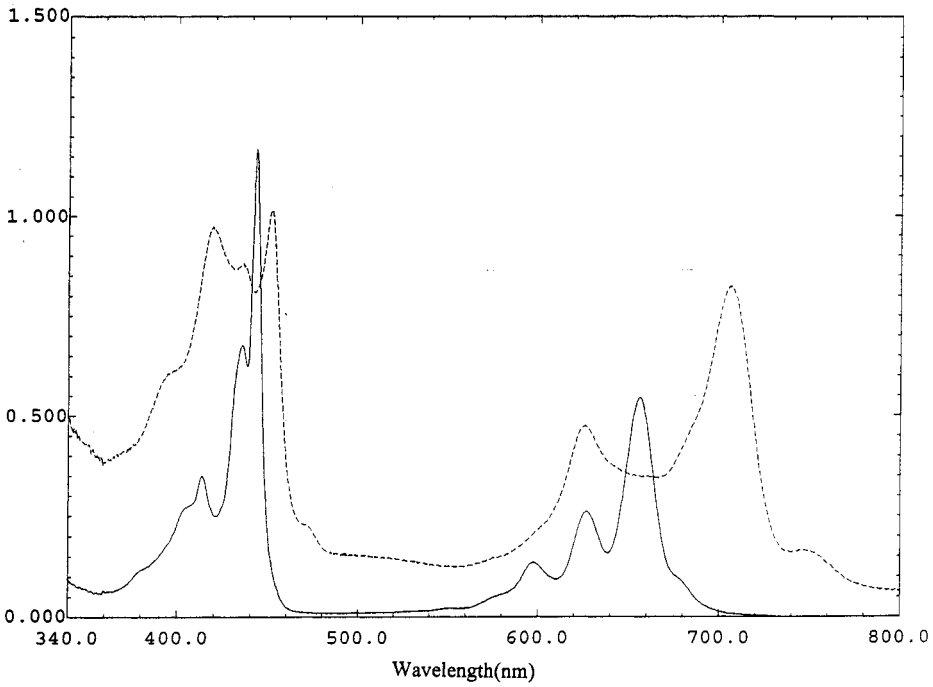
Scheme 1. Reaction of metal-free phthalocyanines **1**−**4** with PBr_3



No.	R^1	R^2	Formula
1	H	H	H_2(pc)
2	H	*t*-Bu	H_2({*t*-Bu}$_4$pc)
3	C_3H_7	C_3H_7	H_2({C_3H_7}$_8$pc)
4	C_5H_{11}	C_5H_{11}	H_2({C_5H_{11}}$_8$pc)

No.	R^1	R^2	Formula
5	H	H	PO(tbc)
6	H	*t*-Bu	PO({*t*-Bu}$_4$tbc)
7	C_3H_7	C_3H_7	PO({C_3H_7}$_8$tbc)
8	C_5H_{11}	C_5H_{11}	PO({C_5H_{11}}$_8$tbc)

Figure 1. UV/Vis spectra of PO(tbc) (**5**) in pyridine (———) and neat trifluoroacetic acid (TFA) (------)



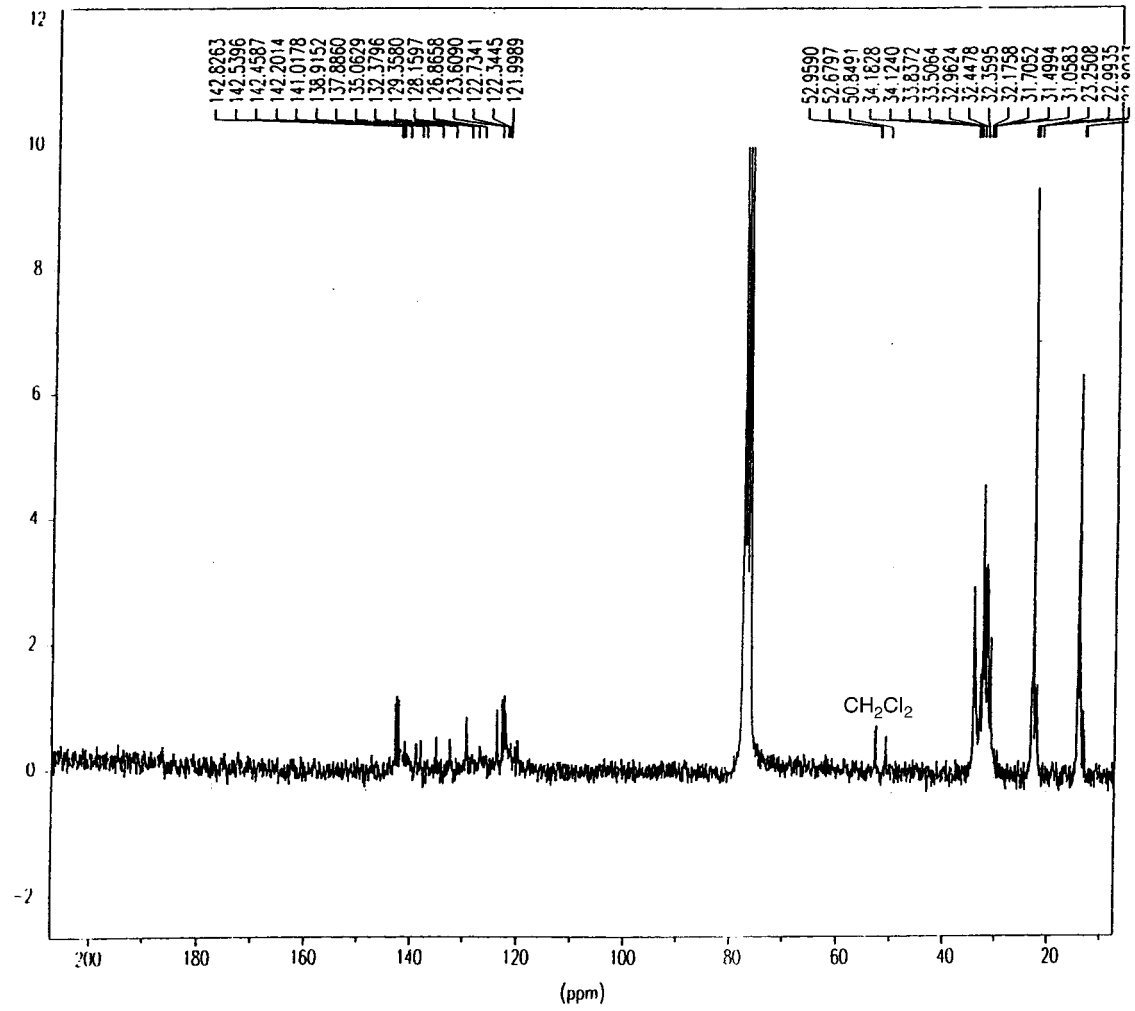
The ^{1}H-NMR spectrum of **5** in [D_5]pyridine features two groups of multiplets, attributable to the internal (Ha, Ha′, Hc, Hc′) and external (Hb, Hb′, Hd, Hd′) aromatic protons, respectively, of the tbc ring (see Scheme 1). A similar pattern of resonances was reported for [Ge(tbc)](OH) in D_2SO_4 by Fujiki et al.[12] Owing to the coupling of the protons in the benzene ring of the tbc macrocycle, it is difficult to distinguish the unsubstituted tbc macrocycle and pc macrocycle by ^{1}H NMR, since the latter also displays two groups of multiplets for the internal (H1, H4) and external (H2, H3) aromatic protons of the pc ring.[14] Liu et al.[13] also reported the ^{1}H-NMR spectrum of the tetrasubstituted tbc complex {HP[(OPr)$_4$tbc]}(OH). However, due to the tetrasubstitution of the tbc complex, a mixture of isomers was inevitably obtained, as is normally found for tetrasubstituted phthalocyanines,[15] and thus only two groups of signals for the benzene protons could be observed. As a result, it is difficult to ascertain the structure of the tbc macrocycle on the basis of its ^{1}H-NMR spectrum. Likewise, the ^{1}H-NMR spectrum of the tetrasubstituted complex **6** features an analogous resonance pattern for the aromatic protons of the macrocycle as that seen for the compound {HP[(OPr)$_4$tbc]}(OH).[13]

In order to unambiguously determine the structures of the tbc macrocycles **5**−**8** by ^{1}H NMR, compounds **7** and **8**, bearing symmetrical alkyl substituents at the peripheral positions of the triazatetrabenzcorrole framework, were prepared according to Scheme 1 and their ^{1}H-NMR spectra were recorded in deuteriated pyridine and chloroform, respectively. There are two kinds of non-equivalent isoindolenine units in the tbc macrocycle; as a result, one should observe four aromatic proton signals in the ^{1}H-NMR spectra of compounds **7** and **8**. Indeed, in the case of **8**, four resonance signals in the aromatic region of equal intensity are clearly observed. On the other hand, only three signals are observed in the same region for **7**. However, integration of these signals (ratio 1:2:1) shows that they correspond to the resonances of four kinds of protons. The reason why two of the proton signals are overlapped in **7** as compared to **8** may be due to the different solvents used. The signals attributable to the alkyl groups in **7** and **8** are multiplets, in contrast to the corresponding signals of the phosphorus phthalocyanines **11** and **12**. Compounds **11** and **12** show triplets for the terminal protons of the alkyl groups, which is also consistent with the proposed structures.

In the ^{1}H-NMR spectrum of the complex {HP[(OPr)$_4$tbc]}(OH), a singlet was observed at $\delta = 3.3$.[13] This was assigned to the resonance of PO−H together with the counterion H^+. However, none of the tbc complexes reported in this paper showed corresponding signals either in this region or in the high-field region. However, in the ^{1}H-NMR spectrum of the complex {Si(OH)[(C_5H_{11})$_8$-tbc]}(OH), the signal at $\delta = -1.57$ assigned to the axially coordinated OH was invariably observed.[11] The upfield shift of this signal was ascribed to the diamagnetic ring current effect of the tbc macrocycle, in analogy with other macrocycles such as porphyrins[16] and phthalocyanines.[17] The ^{1}H-NMR spectrum of complex {HP[(OPr)$_4$tbc]}(OH) was recorded in [D_6]DMSO.[13] In our experience, [D_6]DMSO is a solvent which tends to contain water, and the signal resulting from traces of water in the solvent also appears at $\delta = 3.3$ as a single peak.[18]

The greater solubility of complexes **6** and **8** allows further investigation of the structure of the tbc macrocycle by ^{13}C-NMR spectroscopy. A DEPT-135 NMR spectrum of **8** in $CDCl_3$ exhibits four signals in the aromatic region, which

Figure 2. ^{13}C-NMR spectrum of {PO[$(C_5H_{11})_8$tbc]}



are in accordance with the proposed structure. Thus, the pentyl substituents in **8** give rise to five signals, which show either well-resolved splitting or at least a shoulder. As expected, a ^{13}C-NMR spectrum of **8** in the same solvent features sixteen signals attributable to the framework carbon atoms of the macrocycle (Figure 2), while for complex **6** many more signals are observed in this region owing to the coexistence of structural isomers. In contrast, only seven and four signals are observed in the ^{13}C-NMR spectra of the corresponding phosphorus phthalocyanines **10** and **12**, respectively, due to the framework carbon atoms of the macrocycles.

The ^{31}P-NMR spectra were also recorded for the phosphorus tbc complexes **6** and **8** and the corresponding phthalocyanines **10** and **12**. The proton-decoupled ^{31}P-NMR signal observed for each compound appears between $\delta = -164$ and -189, and this range is typical for six-coordinated phosphorus(V) compounds.[19] In tbc complexes **6** and **8**, the oxygen atom can reasonably be regarded as a bidentate ligand in that it is doubly bonded to the phosphorus(V) atom. Obviously, if the coordinated P atoms in **6** and **8** exist as trivalent P^{3+} and the complexes adopt the formula [HP(tbc)](OH) as suggested in the literature,[13] one should observe a distinctly different signal for the coordinated P atom compared to that in the corresponding phthalocyanine complexes. It seems unreasonable to consider the lone-pair electrons on P^{III} as another axial ligand opposite to OH in the complex {HP[$(OPr)_4$tbc]}(OH).[13] In the ^{31}P-NMR spectra of **6** and **8**, besides the main signal, a second minor signal close to the main one is also observed, indicating that a different coordination environment for P^V may exist. This may be associated with a partial protonation of the axially coordinated oxygen atom by traces of acid present in the solvent (vide supra). Indeed, we found that electronic spectra of pure **6** and **8** dissolved in $CHCl_3$ solution show the presence of at least two species. Moreover, an acid/base effect on the ^{31}P-NMR spectrum of the complex {HP[$(OPr)_4$tbc]}(OH) has been observed.[13] However, protonation at the axial oxygen atom does not lead to an observable effect on the ^{1}H- and ^{13}C-NMR spectra.

The proposed structures for the tbc complexes **5**−**8** are also supported by their IR spectra. A P=O stretching band, observed in the range $\tilde{\nu} = 1281-1298$ cm^{-1} in the IR spectra of complexes **5**−**8**, was not present in the spectra of

complexes **9**–**12**. In the latter complexes, ν_{P-OH} was observed near 940 cm^{-1}, while the ν_{PO-H} appeared in the range 3431–3468 cm^{-1}.

The reported tbc macrocycle complexes have generally been formed by reduction of the corresponding metal phthalocyanines with reagents such as $NaBH_4$, H_2Se, or Si_2Cl_6.[11][12] The mechanism for the formation of the tbc macrocycles remains unclear. On the other hand, all attempts to obtain the metal-free tbc macrocycle by reducing the metal-free phthalocyanine have been unsuccessful.[11][12] PBr_3 is known as a reducing agent, and from this point of view, it can reasonably be postulated that phosphorus phthalocyanine must be formed initially in the reaction, and then reduced by excess PBr_3 to the corresponding tbc macrocycles **5**–**8**. This was ascertained by conducting an experiment in which **10** was treated with PBr_3 in pyridine, whereupon **6** was obtained as the only product. However, the valence state of the coordinated phosphorus atom in the postulated intermediate phthalocyanine was not clear.

For the insertion reaction of PBr_3 into octaethylporphyrin, a phosphorus(III) porphyrin species identified on the basis of its UV/Vis spectrum was proposed, but all attempts to isolate the compound were unsuccessful.[4a][10] On the other hand, in reactions of PBr_3 with tetraarylporphyrins, the phosphorus(III) porphyrin was not observed by UV/Vis spectrophotometry at any stage during the course of the reaction.[20] To the best of our knowledge, no phosphorus(III) porphyrin complexes have been prepared to date. In order to investigate the possibility of preparing phosphorus(III) phthalocyanines, as well as with a view to characterizing the intermediate phosphorus phthalocyanines in the aforementioned reaction of tbc complexes, dilithium phthalocyanine Li_2(pc) was treated with PBr_3 under less vigorous conditions, e.g. at room temperature.[21] When the reaction was carried out in neutral solvents such as acetone, THF or DMF, only metal-free phthalocyanine H_2(pc) was obtained. In contrast, when pyridine was used as the solvent, a phosphorus phthalocyanine species could be detected by its UV/Vis spectrum immediately after the addition of PBr_3 to the mixture of Li_2(pc) and pyridine. The resulting complex was isolated by chromatography and further characterized by its mass spectrum as [P(OH)$_2$(pc)](OH). However, if the reaction was allowed to proceed for a slightly longer time, e.g. 15 min, traces of the tbc macrocycle **5** could also be detected by UV/Vis spectroscopy. Similar results were obtained using $Li_2[(C_5H_{11})_8pc]$ or Li_2(*t*Bu$_4$pc) in place of unsubstituted Li_2(pc). It seems that phthalocyanines, like porphyrins,[22] cannot support a coordinated phosphorus atom in the +III oxidation state. On the other hand, because the radius of P^V is too small compared to the radius of the internal hole of the phthalocyanine ring, the resulting phosphorus(V) phthalocyanine species are more readily susceptible to a ring-contraction reaction, leading to the triazatetrabenzcorrole macrocycle. Further investigations are required to elucidate the reaction mechanism.

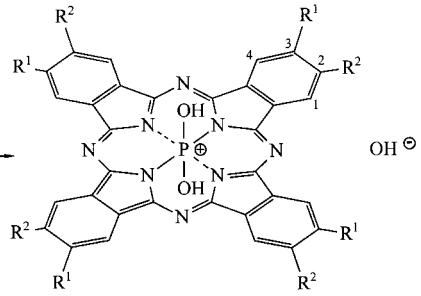
Phosphorus(V) phthalocyanines are seemingly as yet unknown. However, it has been reported that chromatography of the reaction mixture containing "PcP^{III}" yielded a small amount of a blue material, the UV/Vis spectrum of which suggested the formation of "$[PcP^VX_2]^+$".[7] No further characterization was carried out on this complex.[7] Liu et al.[13] also reported to have obtained a phosphorus(V) phthalocyanine complex [P(OPr)$_4$(OH)$_2$(pc)](OH) by the same method, but only its UV/Vis spectrum was reported. In other words, no well-characterized phosphorus phthalocyanines are known in the literature.

During work-up of the reaction mixtures containing the phosphorus tbc complexes **5**–**8** according to the procedure described in the Experimental Section, no blue compounds were isolated except for small amounts of unreacted metal-free phthalocyanines. Hence, we investigated the synthesis of phosphorus phthalocyanines by alternative routes. In a first experiment, PBr_5 was used as the phosphorus source in an attempted reaction with H_2(pc) in pyridine. However, even under reflux conditions and after a long period of time (24 h), no species other than the starting material could be observed either by UV/Vis spectrophotometry or TLC, indicating that for the insertion reaction into phthalocyanine ligands, P^{III} is much more effective than P^V. This is in agreement with reports on the insertion of phosphorus into octaalkylporphyrin ligands, where it was also found that P^{III} was much more effective than P^V.[4a][10]

When $POBr_3$ was used instead of PBr_5 in the reaction with H_2(pc) under the same conditions, complex **9** was obtained in moderate yield. The alkyl-substituted complexes **10**–**12** can be obtained analogously by treatment of **2**–**4** with $POBr_3$, but in much shorter times (Scheme 2). A prolonged reaction time resulted in the formation of water-soluble species, which were difficult to purify. In view of the fact that most phosphorus(V) porphyrin derivatives can be readily obtained by treating the appropriate ligand with $POCl_3$,[23] this reagent was also used as a phosphorus source for the insertion reaction. However, only the *tert*-butyl-substituted complex **10** could be obtained by refluxing H_2(*t*Bu$_4$pc) (**2**) in pyridine for 24 h in the presence of excess $POCl_3$. With the metal-free phthalocyanines **1**, **3** and **4**, no insertion reaction could be achieved, even after a prolonged reaction time. Evidently, $POBr_3$ is much more effective as a phosphorus source for the insertion of phosphorus into phthalocyanine ligands than $POCl_3$. There is no known similar method for the preparation of phosphorus porphyrins. It is merely known that PBr_3 is more reactive than PCl_3 in the same reactions. The reason why only complex **10** could be obtained in the presence of $POCl_3$ might be ascribed to the better solubility of H_2(*t*Bu$_4$pc) in pyridine, whereas the other metal-free phthalocyanines used in this work are essentially insoluble in pyridine.

The most commonly employed method for the preparation of metal phthalocyanines is the heating of phthalodinitriles or diiminoisoindolines in high-boiling solvents such as quinoline, in the presence of metal salts.[24] In order to investigate the possibility of preparing phosphorus phthalocyanines by this method, 4,5-dipentyldiiminoisoindoline and 4,5-dipentyldicyanobenzene were treated with

Scheme 2. Reaction of metal-free phthalocyanines **1**−**4** with $POBr_3$ and $POCl_3$



No.	R^1	R^2	Formula
9	H	H	$[P(OH)_2(pc)](OH)$
10	H	*t*-Bu	$[P(OH)_2(\{t\text{-Bu}\}_4pc)](OH)$
11	C_3H_7	C_3H_7	$[P(OH)_2(\{C_3H_7\}_8pc)](OH)$
12	C_5H_{11}	C_5H_{11}	$[P(OH)_2(\{C_5H_{11}\}_8pc)](OH)$

PBr_3 in quinoline and dimethylaminoethanol, respectively, under reflux. However, neither phthalocyanines nor triazatetrabenzcorroles were obtained under the described conditions. From these preliminary results, it seems that it is not easy to form the corresponding phosphorus phthalocyanines by the commonly used method.

The phosphorus(V) phthalocyanines **9**−**12** were characterized by spectroscopic methods as well as by elemental analysis (see Experimental Section). In contrast to the corresponding phosphorus(V) triazatetrabenzcorroles **5**−**8**, the phosphorus(V) phthalocyanines **9**−**12** exhibit the typical UV/Vis spectra of metal phthalocyanines. Two strong absorptions are observed, one in the visible region at 600−700 nm (Q band) (see Experimental Section) and the other at 300−350 nm (Soret band). The ^{1}H-NMR spectra are also in agreement with the structure assigned to phthalocyanine macrocycles. For example, in contrast to the spectra of the corresponding tbc complexes **7** and **8**, the ^{1}H-NMR spectra of both the phthalocyanine complexes **11** and **12** show a single peak attributable to the aromatic protons. However, the OH protons in neither the ligands nor the counterions of the complexes were observed, owing to rapid exchange with trace amounts of water in the solvent. Similar phenomena are commonly observed for dihydroxyphosphorus(V) porphyrin hydroxide derivatives.[4a][20]

Although the volatility of these ionic compounds **9**−**12** is very low, the FAB technique was effective in obtaining their mass spectra. For most of the compounds prepared, molecular ion peaks were observed, albeit with moderate intensities, together with intense fragment ion peaks corresponding to the cationic phthalocyanine species. The IR spectra of all the complexes show typical vibration absorptions for P−OH in the range 893−941 cm^{-1} and for PO−H around 3431 cm^{-1}.

Both the phosphorus(V) triazatetrabenzcorroles **5**−**8** and the phthalocyanines **9**−**12** show reversible spectral changes at acidic pH. For example, Figures 3a and 3b show the spectral changes that occur upon addition of HCl to complexes **6** and **10** in DMF. It can be seen that the Q bands of these complexes are red-shifted, and that two species exist for the respective complexes over the pH ranges studied. For **10**, it can reasonably be postulated that the red-shifted limiting spectrum (Figure 3b) is due to the species $[P(t\text{Bu}_4pc)(OH)(OH_2)]^{2+}$. Protonation at the *meso*-nitrogen atoms of the phthalocyanine molecules, e.g. from mono- to triprotonated forms, will result in a loss of symmetry of the molecule, and thus the Q bands of the resulting species should show a strong splitting.[25][26] However, no splitting was observed for the Q band of the limiting spectrum of **10**. It would be impossible to form the tetraprotonated species at the pH of the solution, although the tetraprotonated phthalocyanine would also display only one main Q band.[27] By the same reasoning, the limiting spectrum of complex **6** in Figure 3a is probably due to the species $[P(OH)(t\text{Bu}_4tbc)]^+$, where the proton resides on the oxygen atom.

In principle, $[P(OH)_2(t\text{Bu}_4pc)]^+$ could lose a proton to give neutral $[P(O)(OH)(t\text{Bu}_4pc)]$. However, complexes **6** and **10** are insensitive to bases in solution; no detectable spectral changes were observed in the presence of Et_3N in DMF. However, if complex **6** were to exist as $[P(OH)(t\text{Bu}_4tbc)]H$, in analogy with the structure suggested in the literature,[13] the spectrum of a solution of the complex would show base sensitivity. Thus, one should have observed a blue shift of the Q band in the presence of base.

Conclusions

Complexes produced by treating the metal-free phthalocyanines **1**−**4** with PBr_3 have been characterized by spectroscopic methods as oxophosphorus(V) triazatetrabenzcorroles **5**−**8**, which arise from the reduction of intermediate phosphorus(V) phthalocyanine species with excess PBr_3. The reduction could be an N extrusion by nucleophilic attack at the *meso*-nitrogen atom with formation of a $[PNBr_3]^-$ species. The central coordinated phosphorus atom in **5**−**8** was identified as being P^V rather than P^{III}, on the basis of MS, ^{31}P NMR, and IR evidence, as well as from the changes in the UV/Vis spectra of the complexes that occur upon addition of acid. For comparison, phosphorus phthalocyanines **9**−**12** were prepared by treating the phthalocyanines **1**−**4** with $POBr_3$ or $POCl_3$. The resulting complexes **9**−**12** were characterized in detail for the first time.

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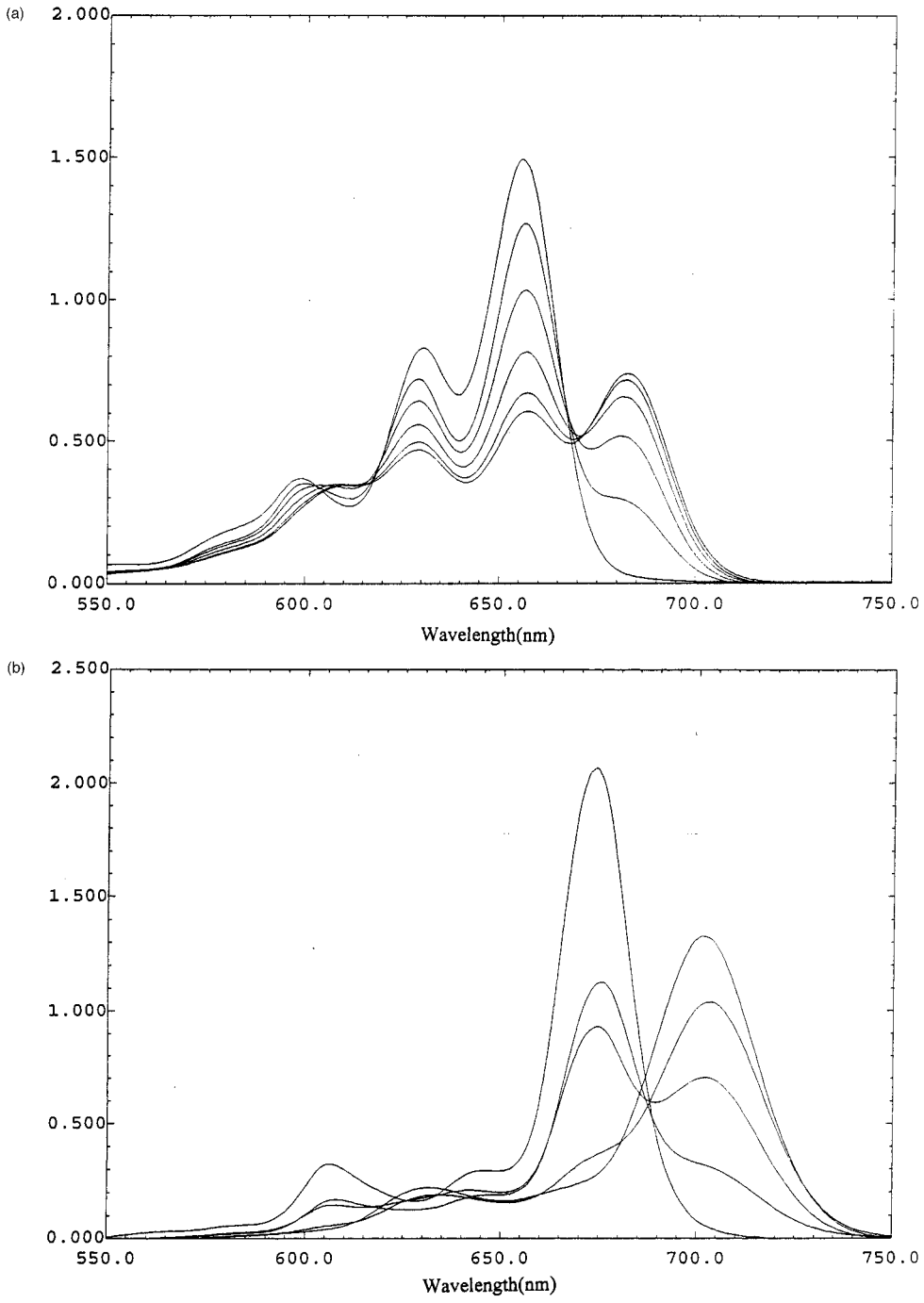
Experimental Section

All solvents were dried and distilled prior to use. Pyridine was distilled from calcium hydride under nitrogen. $H_2(pc)$ (**1**) was prepared by the literature method.[28] Tetra-*tert*-butylphthalocyanine $[H_2(t\text{Bu}_4pc)]$ (**2**), 2,3,9,10,16,17,23,24-octapropylphthalocyanine $\{H_2[(C_3H_7)_8pc]\}$ (**3**), and 2,3,9,10,16,17,23,24-octapentylphthalocyanine $\{H_2[(C_5H_{11})_8pc]\}$ (**4**) were prepared by refluxing the appropriate diiminoisoindoline in dimethylaminoethanol and purified according to the methods we have described previously.[29] The corre-

Figure 3. Visible absorption spectral changes of (a) [PO(tBu$_4$tbc)] (**6**) and (b) [P(OH)$_2$(tBu$_4$pc)](OH) (**10**) in DMF upon stepwise addition of aqueous HCl up to the limiting spectra; the final concentration of acid is 8.4×10^{-2} mol/l vs. 2.4×10^{-5} mol/l [PO(tBu$_4$tbc)] (**6**) and 1.6×10^{-5} mol/l [P(OH)$_2$(tBu$_4$pc)](OH) (**10**), respectively (reading from the lower to the upper trace at 681 and 702 nm for the respective complexes)



sponding dilithium phthalocyanines were prepared by the procedure described by Linstead et al.[30] All reactions were carried out under nitrogen, and the subsequent isolation and purification procedures were carried out under ambient conditions. UV/Vis absorption spectra were recorded with a Shimadzu UV-365 spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were recorded with a Bruker AC 250 spectrometer operating at 250 and 62.5 MHz, respectively, and ^{31}P-NMR spectra with a Bruker DRX 250. Mass spectra were recorded with a Varian MAT 711 in FAB mode with 3-nitrobenzyl alcohol (NBM) as matrix. FT-IR spectra were obtained using KBr plates with an IFS 48 spectrophotometer. Elemental analyses were performed with Carlo Erba Elemental Analysers 1104, 1106.

Oxophosphorus(V) Triazatetrabenzcorrole [PO(tbc) (**5**)]: A mixture of H$_2$(pc) (**1**) (1.2 g, 2.34 mmol) and pyridine (20 ml) was placed in a 50-ml three-necked round-bottomed flask, equipped with a reflux condenser and a gas inlet tube. A solution of PBr$_3$ (6.5 ml, 70.2 mmol) in pyridine (10 ml) was then added and the resulting mixture was heated at 90−100°C under stirring for 1.5 h.

After cooling to room temperature, the mixture was poured into water, the resulting suspension was filtered, and the collected solid was washed thoroughly with water. The crude product was dissolved in pyridine and purified by column chromatography on neutral alumina using a mixture of pyridine and ethanol (1:1) as eluent. The unreacted H_2(pc), which is only sparingly soluble in pyridine, stayed at the top of the column. The green band was collected and concentrated to dryness under reduced pressure, affording 0.92 g (72%) of a deep-green solid. – IR (KBr): $\tilde{\nu}$ = 1614 cm^{-1}, 1541, 1506, 1425, 1342, 1319, 1298 (P=O), 1259, 1119, 1099, 951, 833, 752, 714, 632, 568. – UV/Vis (pyridine): λ_{max} (lg ε) = 656 nm (0.47), 627 (0.22), 597 (0.12), 442 (1.00), 435 (0.58), 413 (0.30). – FAB-MS: *m/z* (%): 545.2 [M^+] (3). – ^{1}H NMR ([D_5]pyridine): δ = 8.16–8.31 (m, 8 H, tbc ring external H), 9.37–9.54 (m, 8 H, tbc ring internal H). – $C_{32}H_{16}N_7PO \cdot H_2O$: calcd. C 68.21, H 2.86, N 17.40; found C 70.96, H 3.34, N 14.96.

Oxophosphorus(V) 4,11,18,25-Tetra-tert-butyltriazatetrabenzcorrole [PO(*t*Bu_4tbc) (**6**)]: H_2(*t*Bu_4pc) (150 mg) was treated with PBr_3 (0.6 ml) following the procedure described for the preparation of complex **5**. The crude product was purified by column chromatography on neutral alumina using chloroform as eluent. The first faintly blue fraction contained unreacted H_2(*t*Bu_4pc), while the green fraction containing the bulk of the product was collected and concentrated under reduced pressure to give 120 mg (77%) of a dark blue-purple shiny solid consisting of a mixture of isomers. – IR (KBr): $\tilde{\nu}$ = 2961 cm^{-1}, 2905, 1620, 1514, 1429, 1418, 1366, 1332, 1283 (P=O), 1255, 1150, 1103, 1060, 966, 825, 764, 708, 660. – UV/Vis (pyridine): λ_{max} (lg ε) = 658 nm (0.49), 632 (0.25), 601 (0.12), 445 (1.00), 415 (0.31). – FAB-MS: *m/z* (%): 769.4 [M^+] (100), 922.2 [M^+ + NBM] (80), 754.4 [$M^+ - CH_3$] (50), 739.4 [$M^+ - 2CH_3$] (30). – ^{1}H NMR ([D_8]THF): δ = 9.21–10.07 (m, 8 H, $H_{arom.}$), 8.33–8.87 (m, 4 H, $H_{arom.}$), 2.06–2.15 (m, 36 H, *t*Bu). – ^{13}C NMR ($CDCl_3$): δ = 31.42–32.09 (CH_3), 35.90–36.30 [$C(CH_3)_3$], 118.12, 118.58, 119.13, 119.98, 122.19, 122.60, 122.74, 123.75, 126.77, 127.52, 128.52, 130.93, 137.92, 139.17, 152.13, 152.78. – ^{31}P NMR ($CDCl_3$): δ = –186.7. – $C_{48}H_{48}N_7PO$: calcd. C 74.88, H 6.28, N 12.73; found C 69.40, H 6.38, N 12.72.

Oxophosphorus(V) 4,5,11,12,18,19,25,26-Octapropyltriazatetrabenzcorrole {PO[$(C_3H_7)_8$tbc] (**7**)}: H_2[$(C_3H_7)_8$pc] (50 mg) was treated with PBr_3 (0.2 ml) according to the procedure described for the preparation of complex **5**. A deep-green solid was obtained; yield 34 mg (65%). – IR (KBr): $\tilde{\nu}$ = 2957 cm^{-1}, 2932, 1626, 1543, 1462, 1418, 1364, 1340, 1281 (P=O), 1277, 1124, 1092, 901, 833, 764, 575. – UV/Vis (pyridine): λ_{max} (lg ε) = 662 nm (0.49), 636 (0.26), 604 (0.12), 447 (1.00), 417 (0.32). – FAB-MS: *m/z* (%): 881.5 [M^+] (100), 837.4 [$M^+ - H - C_3H_7$] (18), 1034.5 [M^+ + NBM] (40). – ^{1}H NMR ([D_5]pyridine): δ = 9.83 (s, 2 H, $H_{arom.}$), 9.73 (s, 4 H, $H_{arom.}$), 9.63 (s, 2 H, $H_{arom.}$), 3.14–3.30 (m, 16 H, CH_2), 1.89–2.21 (m, 16 H, CH_2), 1.11–1.31 (m, 24 H, CH_3). – $C_{56}H_{64}N_7PO$: calcd. C 76.52, H 7.31, N 11.11; found C 74.55, H 7.51, N 10.51.

Oxophosphorus(V) 4,5,11,12,18,19,25,26-Octapentyltriazatetrabenzcorrole {PO[$(C_5H_{11})_8$tbc] (**8**)}: H_2[$(C_5H_{11})_8$pc] (50 mg) was treated with PBr_3 (0.2 ml) in pyridine and the crude product was purified according to the procedure described for complex **6** to afford 32 mg (63%) of a deep-green solid with a purple lustre. The product was further purified by dissolving it in a minimum volume of CH_2Cl_2 and reprecipitating it by the addition of CH_3OH. – IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1}, 2928, 1625, 1514, 1462, 1425, 1342, 1301, 1284 (P=O), 1195, 1109, 887, 827, 731, 594. – UV/Vis (pyridine): λ_{max} (lg ε) = 662 nm (0.48), 637 (0.26), 605 (0.11), 448 (1.00), 418 (0.31). – FAB-MS: *m/z* (%): 1105.1 [M^+] (100), 1258.2 [M^+ + NBM] (60). – ^{1}H NMR ($CDCl_3$): δ = 9.57 (s, 2 H, $H_{arom.}$), 9.56 (s, 2 H, $H_{arom.}$), 9.54 (s, 2 H, $H_{arom.}$), 9.45 (s, 2 H, $H_{arom.}$), 3.22–3.47 (m, 16 H, CH_2), 2.00–2.40 (m, 16 H, CH_2), 1.65–1.84 (m, 32 H, CH_2), 1.10–1.15 (m, 24 H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 13.96–14.35, 22.08–23.25, 31.05–31.70, 32.17–32.96, 33.50–34.18 (alkyl); 121.99, 122.34, 122.73, 123.60, 126.86, 128.15, 129.35, 132.37, 135.06, 137.88, 138.91, 141.01, 142.20, 142.46, 142.54, 142.82. – ^{31}P NMR ($CDCl_3$): δ = –189.41. – $C_{72}H_{96}N_7PO$: calcd. C 78.15, H 8.74, N 8.86; found C 76.60, H 8.58, N 8.43.

Dihydroxyphosphorus(V) Phthalocyanine Hydroxide {[$(OH)_2$-P(pc)](OH) (**9**)}: $POBr_3$ (1.0 g) was added to a suspension of H_2(pc) (50 mg) in pyridine (30 ml) and the stirred mixture was heated to 80–90°C overnight. After cooling to room temperature, the mixture was poured into water (100 ml), and the resulting precipitate was collected by vacuum filtration and washed thoroughly with water. The crude product thus obtained was taken up in pyridine and purified by chromatography on silica gel using a mixture of pyridine and methanol (1:1) as eluent. The blue fraction containing the bulk of the product was collected and the solvents were removed under reduced pressure to give 38 mg (65%) of a blue solid. – IR (KBr): $\tilde{\nu}$ = 3431 cm^{-1} (PO–H), 1724, 1659, 1472, 1433, 1385, 1334, 1312, 1124, 1083, 941 (P–OH), 914, 756, 730, 577. – UV/Vis (pyridine): λ_{max} (lg ε) = 669 nm (1.00), 640 (0.14), 602 (0.16), 353 (0.32). – FAB-MS: *m/z* (%): 594.2 [M^+] (5), 576.8 [$M^+ - OH$] (20). – ^{1}H NMR ([D_5]pyridine): δ = 9.30–9.38 (m, 8 H, pc ring internal H), 8.11–8.18 (m, 8 H, pc ring external H). – $C_{32}H_{19}N_8PO_3$: calcd. C 64.65, H 3.22, N 18.85; found C 62.69, H 3.16, N 18.04.

Dihydroxyphosphorus(V) 2,9,16,23-Tetra-tert-butylphthalocyanine Hydroxide {[$P(OH)_2$(*t*Bu_4pc)](OH) (**10**)}: $POCl_3$ (8 ml) was added dropwise to a solution of H_2(*t*Bu_4pc) (50 mg) in pyridine (20 ml) and the resulting mixture was heated under reflux for 24 h. The cooled solution was then poured slowly onto ice and the precipitate thus obtained was collected by centrifugation and washed thoroughly with water. The crude product was dissolved in a minimum volume of chloroform and chromatographed on silica gel. Elution with chloroform removed any H_2(*t*Bu_4pc) present. The desired compound was then eluted as a deep-blue band using chloroform/methanol (7:3). Removal of the solvents resulted in 35 mg (63%) of a deep-blue solid. – IR (KBr): $\tilde{\nu}$ = 3441 cm^{-1} (PO–H), 2961, 1620, 1483, 1413, 1365, 1330, 1285, 1257, 1157, 1105, 1084, 941 (P–OH), 752, 557. – UV/Vis (pyridine): λ_{max} (lg ε) = 677 nm (1.00), 648 (0.15), 609 (0.16), 353 (0.40). – FAB-MS: *m/z* (%): 800.8 [$M^+ - OH$] (100), 782.8 [$M^+ - H - 2OH$] (30), 737.8 [$M^+ - H - 2OH - 3CH_3$] (15), 723.2 [$M^+ - H - 2OH - 4CH_3$] (10). – ^{1}H NMR ([D_8]THF): δ = 7.91–9.56 (m, 12 H, $H_{arom.}$), 2.09–2.13 (36 H, *t*Bu). – ^{13}C NMR ($CDCl_3$): δ = 31.04–31.88 (CH_3), 35.90–36.05 [$C(CH_3)_3$], 119.02, 122.77, 128.98, 131.14, 133.74, 146.45, 154.97. – ^{31}P NMR ($CDCl_3$): δ = –166.07. – $C_{48}H_{51}N_8PO_3$: calcd. C 70.40, H 6.28, N 13.68; found C 68.70, H 6.24, N 14.25.

Dihydroxyphosphorus(V) 2,3,9,10,16,17,23,24-Octapropylphthalocyanine Hydroxide {$P(OH)_2$[$(C_3H_7)_8$pc]}(OH) (**11**): The procedure used for the preparation and purification of complex **11** was as that described for complex **9**, except that the reaction time was 2.5 h instead of overnight. A blue solid was obtained in a yield of 58%. – IR (KBr): $\tilde{\nu}$ = 3433 cm^{-1} (PO–H), 2959, 2932, 1622, 1533, 1458, 1421, 1342, 1092, 905 (P–OH), 750, 476. – UV/Vis (pyridine): λ_{max} (lg ε) = 684 nm (1.00), 654 (0.15), 615 (0.16), 351 (0.31). – FAB-MS: *m/z* (%): 930.4 [M^+] (2), 913.4 [$M^+ - OH$] (10), 895.4 [$M^+ - H - 2OH$] (3). – ^{1}H NMR ([D_5]pyridine): δ = 9.48 (s, 8

H, $H_{arom.}$), 2.99 (t, 16 H, J = 8.27 Hz, CH_2), 1.74−1.83 (m, 16 H, CH_2), 0.99 (t, 24 H, J = 7.75 Hz, CH_3). − $C_{56}H_{67}N_8PO_3$: calcd. C 72.23, H 7.25, N 12.03; found C 68.08, H 6.52, N 11.74.

Dihydroxyphosphorus(V) 2,3,9,10,16,17,23,24-Octapentylphthalocyanine Hydroxide ({$P(OH)_2$[$(C_5H_{11})_8$pc](OH)} (**12**): $POBr_3$ (1.0 g) was added to a suspension of H_2[$(C_5H_{11})_8$pc] (50 mg) in pyridine (15 ml) and the mixture was heated to 90−100°C under stirring for 1.5 h. After cooling to room temperature, the mixture was poured into water and the resulting precipitate was collected by centrifugation and washed thoroughly with water. The crude product thus obtained was dissolved in a minimum volume of chloroform and chromatographed on silica gel. Elution with chloroform removed a blue band containing unreacted H_2[$(C_5H_{11})_8$pc]. The desired product was then eluted as a deep-blue band using $CHCl_3$/CH_3OH (7:3). The solvents were removed under reduced pressure to give 30 mg (56%) of a deep-blue solid. − IR (KBr): $\tilde{\nu}$ = 3468 cm^{-1} (PO−H), 2957, 2930, 1622, 1531, 1462, 1423, 1342, 1049, 893 (P−OH), 750, 734. − UV/Vis (pyridine): λ_{max} (lg ε) = 685 nm (1.00), 654 (0.14), 615 (0.16), 351 (0.29). − FAB-MS: *m/z* (%): 1138.3 [M^+ − OH] (65), 1134.8 [M^+ − OH − 2 H] (40), 1119.6 [M^+ − 2OH − H] (15). − ^{1}H NMR ([D_8]THF): δ = 9.28 (s, 8 H, $H_{arom.}$), 3.29 (t, 16 H, J = 7.99 Hz, CH_2), 1.99−2.11 (m, 16 H, CH_2), 1.53−1.72 (m, 32 H, CH_2), 1.06 (t, 24 H, J = 7.01 Hz, CH_3). − ^{13}C NMR ($CDCl_3$): δ = 14.12, 22.68, 31.15, 32.31, 34.01, 122.76, 131.88, 144.67, 146.35. − ^{31}P NMR ($CDCl_3$): δ = −163.99. − $C_{72}H_{99}N_8PO_3$: calcd. C 74.83, H 8.63, N 9.70; found C 75.04, H 8.68, N 9.62.

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