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# Synthesis and X-ray crystal structures of imido and ureato derivatives of titanium(IV) phthalocyanine and their application in the catalytic formation of carbodiimides by metathesis from isocyanates<sup>†</sup>

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The imido titanium phthalocyanine complex [PcTi(NDip)] (Dip = 2,6-diisopropylphenyl) **2a** was synthesized from [PcTiO] **1** and one eq. of DipNCO. Due to the steric demand of the Dip group, addition of another isocyanate molecule to the Ti==N functionality of **2a** does not occur even at high molar ratios of DipNCO. However, **1** reacts with 2 eq. of arylisocyanates containing sterically less demanding aryl groups producing N,N'-diarylureatotitanium(IV)phthalocyanines [PcTi{ $\kappa^2$ -(NR)C(O)(N'R)] (R = *p*-tolyl (Tol) **3a** or mesityl (Mes) **3b**). The N,N' coordination (III) of the ureato ligand in **3a** and **3b** was proven by a single set of resonances for the aryl groups in their <sup>1</sup>H-NMR spectra. An N,O coordination (IV) can therefore be excluded. This is also confirmed by the X-ray crystal structure of **3a**. Upon heating [PcTiO] and an excess of aryl isocyanates for 6 days, a steady evolution of CO<sub>2</sub> was observed and a white precipitate, identified as the corresponding diarylcarbodiimides (V), could be isolated. Therefore this reaction was applied in the metathetic conversion of two isocyanate molecules into diarylcarbodiimides (V) and CO<sub>2</sub>. Additionally, imido titanium Pc's **2b** (R = *t*Bu) and **2c** (R = Mes) were prepared by a more general synthetic strategy, reacting the potassium salt of the ligand PcK<sub>2</sub> with appropriate imido titanium precursors.

# Introduction

Titanyl phthalocyanines ([PcTiO]) have found many applications, such as their use in the manufacture of organic photoreceptors in electrographic printing devices<sup>1-5</sup> and in CD-R optical data storage.<sup>6</sup> In this context, surprisingly little is known about the functionalization of the axial oxo group in titanium phthalocyanines (TiPc's). Next to the parent compounds [PcTiO]<sup>7-9</sup> and [PcTiCl<sub>2</sub>],10 other axially substituted TiPc's reported in the literature are oxalato, catecholato, dithiocatecholato<sup>11-13</sup> and chalcogenido derivatives [PcTiX] (X = S, Se, or Te).<sup>14</sup> Recently, we described that [PcTiO] can be activated by reaction with ptolyl isocyanate, and that the assumed intermediate, an N,N'bis-p-tolyl ureato(2-) complex, can be used for protolytic ligand exchange reactions with SH-, OH- and NH-acidic ligands.15 However, the isolation of this valuable ureato key compound in pure form, its full characterization and mechanistic studies, adding proof for terminal imido titanium phthalocyanines as reactive intermediates, have not been accomplished so far. This report describes the isolation of pure ureato and first imido titanium

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phthalocyanines, their reactions and thermochemistry and their use in catalysis.

Macrocycle-supported imido complexes such as porphyrins and cumulenes could not be prepared by the direct reaction of the corresponding titanium oxo species with RNCO. For porphyrins, the imido complex [(TTP)Ti(NR)] (TTP = tetratolylporphyrinato dianion) can be prepared by the reaction of [(TTP)TiCl<sub>2</sub>] with 2 eq. of LiNHR<sup>16,17</sup> or by the reaction of [(TTP)Ti( $\eta^2$ -3-hexyne)] with RNCO or RNCNR.<sup>18</sup> Similarly, the imido porphyrins of other group 4 metals [(TTP)M(NR)] (M = Zr or Hf) could not be prepared from the oxo complexes and tBuNCO but from the reaction of the dichloro complexes with 2 eq. of LiNHR.<sup>19</sup> Another synthetic strategy leading to macrocycle-supported imido titanium complexes is the reaction of alkaline metal ligand salts with imido titanium precursors. Thus the imido complexes  $[(\kappa^4-Me_n \tan)Ti(NtBu)]$  (n = 4 or 8, taa = tetra- or octamethyldibenzotetraaza[14]-annulene) were prepared by the reaction of  $Li_2[Me_ntaa]$  with  $[Ti(NtBu)Cl_2(tBupy)_2]$ .<sup>20</sup> A porphyrin analogue was synthesized by a similar procedure.<sup>21</sup> Using this compound as starting material, Mountford et al.22 prepared the arylimido derivatives  $[(\kappa^4 - Me_4 taa)Ti(NR)]$  (R = Ph, Tol). They found that the reaction of these compounds with RNCO produces symmetric and asymmetric N,N'-diarylureato compounds.  $[(\kappa^4-Me_4taa)Ti\{\kappa^2-$ (NTol)C(O)(N'Tol) could also be obtained by the reaction of the oxo derivative with TolNCNTol.23

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As one of the synthetic strategies for the replacement of the oxo functionality and generating an organoimido group, we chose the metathesis of [PcTiO] **1** with organic isocyanates ArNCO (Scheme 1). This metathetic transformation was found to depend largely on the size of the aryl group. For the bulky 2,6-diisopropylphenyl group, the imido complex [PcTi(NDip)] **2a** was the final product. For the sterically less demanding groups, R = Tol or mesityl, the *N*,*N*'-diarylureato complexes [PcTi{ $\eta^2$ -(NR)C(O)(N'R)}] (R = Tol **3a** or Mes **3b**), could be isolated in a pure form.



Scheme 1 Reaction of [PcTiO] 1 with different arylisocyanates.

The suggested reaction mechanism (Scheme 2) includes a [2 + 2]-cycloaddition of an isocyanate molecule with the titanyl group forming a CO<sub>2</sub>-adduct (I) as cyclic intermediate. This unstable metallocycle readily loses a molecule of CO<sub>2</sub> forming the corresponding imido complex [PcTi(NR)] (**2a**). In the case of sterically demanding 2,6-diisopropylphenyl isocyanate only one addition step occurs and the imido complex is the final product. Addition of a second isocyanate molecule to the Ti=NDip functionality is hindered because of the high steric demand of the two isopropyl groups. In the case of arylisocyanates containing sterically less demanding aryl groups (Ar = Tol or Mes) a second [2 + 2]-cycloaddition of an isocyanate molecule at the Ti=N-bond



Scheme 2 Suggested mechanism for the reaction of [PcTiO] 1 with arylisocyanates and catalytic carbodiimide formation.

is possible and results in the formation of N,N'-ureato complexes (III). Upon heating of 1 with isocyanates containing smaller substituents for 6 days, a steady evolution of CO<sub>2</sub> was observed and a white precipitate, identified as the corresponding carbodiimide (V), could be isolated. The carbodiimide is presumably formed as a result of slow isomerization of the N,N'- bound ureato complex (III) to the N,O-bound complex (IV) after which IV decomposes into the carbodiimide and [PcTiO] upon cleavage of the Ti–N and Ti–O bonds.<sup>24</sup>

Since the reaction of [PcTiO] with isocyanates only yields imido compounds if very bulky aryl substituents such as Dip are employed, we searched for a more general synthetic strategy for the target molecules [PcTi(NR)]. Mountford et al. showed that the reaction of dilithium salts of various macrocyclic ligands with appropriate imido titanium precursors lead to the desired imido compounds. In order to apply this method to phthalocyanine chemistry, it is crucial to note, that commercially available PcLi<sub>2</sub> commonly contains the not fully lithiated species PcLiH and PcH<sub>2</sub>. While PcLi<sub>2</sub> reacts with titanium precursors in the desired way, PcLiH and PcH<sub>2</sub> do not, and the obtained mixtures can not be separated properly. We therefore tested various lithium bases in the deprotonation of PcH<sub>2</sub> to obtain pure PcLi<sub>2</sub>, but while  $LiN(SiMe_3)_2$  does not complete the reaction, stronger bases such as LiNiPr<sub>2</sub> or BuLi lead to ortho-directed deprotonation of the aromatic system.25,26

On the other hand, we found that the reaction of 2.5 eq. of benzyl potassium with  $PcH_2$  gives pure  $PcK_2$ . The absence of any protonated Pc species is confirmed by MALDI–TOF and UV/vis spectra.  $PcK_2$  was then reacted with titanium imido precursors of the type  $[Ti(NR)Cl_2py_{2-3}]$  in THF. Many such precursors have been described in the literature,<sup>27-29</sup> and we decided to confine ourselves to the use of  $[Ti(NtBu)Cl_2py_3]$  as an alkyl imdo precursor and  $[Ti(NMes)Cl_2py_2]$  as an aryl imido precursor (Scheme 3). We obtained imido titanium phthalocyanines [PcTi(NtBu)] (**2b**) and [PcTi(NMes)] (**2c**), and we believe that our method can be generally applied to synthesize imido titanium phthalocyanines.



Scheme 3 Formation of imido titanium Pc's via insertion.

The <sup>1</sup>H-NMR spectra of **2a–c**, **3a** and **3b** show resonance at the expected chemical shifts, and the integral values are in accordance with the suggested structures. The phthalocyanine unit shows the characteristic AA'BB' pattern in the aromatic region typical for unsubstituted Pc's.<sup>30</sup> The resonances for the eight protons in the 1,4-positions occur at 9.64–9.93 ppm and those for the eight protons in the 2,3-positions at 8.25–8.47 ppm. The typical, strong downfield shift of the aromatic protons of the macrocyle is due to the well-known ring current effect.<sup>13,30</sup> This is also the reason why the signals of the axial ligands, which are perpendicular to the

	First degradation stage			Second degradation stage		
	Temp./°C	Weight loss (%) (calcd.)	Lost unit	Temp./°C	Weight loss (%) (calcd.)	Lost unit
2a	300-420	23.8 (24)	DipN		_	
3a	212-260	16.8 (18)	ToÎNCO	260-520	30.0 (30)	TolN
3b	317-320	19.0 (22)	MesNCO	320-435	34.4 (35)	MesN

Table 1 Thermal analysis data of 2a, 3a and 3b

ring plane, are shifted to higher field. The single set of resonances for the two N-bound aryl groups of the ureato ligand in 3a or 3b reveals that these two aryl groups are equivalent. This suggests the presence of the symmetric N, N'-coordination (III) rather than the unsymmetric N,O-bound one (IV) in solution, which is also supported by the crystal structure of 3a.

The m/z values of the molecular ions of imido- and ureato-TiPc's 2a-c and 3a-b were observed in EI, APCI and MALDI-TOF measurements with the expected isotopic patterns. The molecular ion peak of 1 ( $M^+$  = 576) was not observed in the products. Purity was confirmed by elemental analyses (C, H, N, Ti). The IR spectra of all TiPc's show the typical absorptions of the basic Pc moiety, such as  $v_{C=C}$  at 1608 cm<sup>-1</sup>, while the characteristic Ti=O stretching band ( $v_{Ti=0}$  at 965 cm<sup>-1</sup>) is not observed.<sup>31</sup> Additionally, the vibrations at 1683 cm<sup>-1</sup> (3a) and 1684 cm<sup>-1</sup> (**3b**) can be assigned to the carbonyl group  $(v_{C=0})^{24}$ 

UV/vis spectra of 1, 2a and 3a (Fig. 1) show the characteristic absorptions for metal phthalocyanine.<sup>11–13,31,32</sup> The Q band at  $\lambda_{max}$  = 698 nm is attributed to a  $\pi$ - $\pi$ \* transition. The shoulders at 665 nm and 628 nm can be attributed to vibronic transitions.<sup>33</sup> A second allowed  $\pi - \pi^*$  transition (B band) is observed around 340 nm. Generally, no significant changes are induced in the absorption spectra upon replacement of the titanyl group by imido or ureato ligands. This is attributed to the fact that the absorption energies and patterns arise mainly from the phthalocyanine basic moiety and are only slightly affected by the nature of the axial ligands.<sup>11-13</sup> No significant solvent dependence was observed when the absorption measurements were carried out either in chloronaphthalene, dichloromethane or chloroform.



Fig. 1 UV/vis spectra of 1, 2a and 3a in CHCl<sub>3</sub>.

The stepwise thermal degradation of a Pc molecule may be used to give an idea about its structure.<sup>34</sup> The thermogravimetric



Fig. 2 TGA diagram of 2a.

analysis of 2a (Fig. 2) shows that the molecule loses the imido ligand ([NDip], C<sub>12</sub>H<sub>17</sub>N) in a first degradation step in the temperature range of 300-420 °C. The loss of the ureato ligand in **3a** and **3b** occurs in the temperature range of 220–300 °C within two steps (Fig. 3). The first step can be attributed to the loss of ArNCO molecule via a [2 + 2]-cyclo reversion and formation of an imido complex. The second step is the loss of nitrene fragment [ArN] producing [PcTi]. In addition, the decomposition of the Pc macrocycle starts at about 550 °C, which is common for metalphthalocyanines. The observed weight losses match well with the theoretical values for the supposed decomposition steps (Table 1). This controlled stepwise thermal decomposition will be further exploited to generate highly reactive intermediates [PcTi] and to trap these with added ligands.



Fig. 3 TGA diagram of 3b.

#### Crystal structure of 2a

Single crystals of imido titanium compound 2a could be obtained by controlled cooling of a 1-chloronaphthalene solution. The

Ti–N1	2.056(2)	Ti-N12	2.054(2)
Ti-N22	2.057(2)	Ti-N32	2.063(2
Ti-N41	1.712(2)	N41-C42	1.393(4
C42-N41-Ti	179.0(2)	N41-Ti-N12	106.0(1
N41-Ti-N22	107.7(1)	N12-Ti-N22	85.4(1)
N41-Ti-N1	106.0(1)	N12-Ti-N1	85.2(1)
N22-Ti-N32	84.9(1)	N41-Ti-N31	107.7(1)
N12-Ti-N32	146.3(1)	N22-Ti-N32	84.9(1)
N1-Ti-N32	85.3(1)		

crystal structure of 2a (Fig. 4) shows a very similar coordination geometry to that of its analogue phenylimido titanium tetratoluylporphyrine [(TTP)Ti(NPh)].<sup>16</sup> The geometry around the titanium atom is square-pyramidal with the four isoindoline nitrogen atoms forming the basal plane and the imido group at the apical site. Due to the presence of the axial ligand, the titanium atom is displaced from the plane defined by the four isoindoline nitrogen atoms toward the imido ligand by 0.597 Å. This in turn causes the aromatic system to deviate from planarity and adapt a "saucer"like shape.<sup>35</sup> The imido titanium group is essentially linear with a C42–N41–Ti angle of 179.0(2)°. The slight deviation from 180° is in the typical range for imido titanium compounds.<sup>27</sup> The imido bond length [Ti-N41] is 1.712(1) Å, which corresponds to a Ti-N triple bond. Selected bond lengths and bond angles of 2a are given in Table 2.



Fig. 4 Molecular structure of 2a, H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.

Fig. 5 shows the molecular arrangement in the unit cell of 2a. Due to the  $\pi$ - $\pi$  interactions of the macrocycles the structure consists of closely packed of face-to-face dimers with a distance between two adjacent N<sub>4</sub>-planes of 3.41(1) Å. The arrangement of the molecules as face-to-face dimers is also observed for a modification of [PcTiO]. This packing in 2a is much less dense due to the sterically demanding 2,6-diisopropylphenyl-group, which may explain the better solubility of 2a-c compared to [PcTiO].9,36 However, the two molecules of the dimer are related to each other by a crystallographic inversion centre.

#### Crystal structure of 3a

Suitable crystals for X-ray diffraction of ureato complound 3a could be obtained by controlled cooling of a chlorobenzene solution. The molecular structure of 3a is shown in Fig. 6.



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Fig. 5 The molecular packing of 2a. H atoms are omitted for clarity.

The configuration around the titanium atom is best described as a capped square pyramid with the four isoindoline nitrogen atoms almost lying in one plane. The ureato ligand occupies two neighboring apical coordination sites. The titanium atom in **3a** is more displaced from the  $N_4$  plane (0.763 Å) than in **2a** (0.597 Å). The ureato ligand is bound to the titanium atom in the symmetrical N,N'-coordination (not N,O-coordinated). This confirms the result of 1H-NMR spectroscopy. The metallacycle fragment encloses an obtuse N-C-N angle of 100.5(5)° as well as an acute N-Ti-N angle of 65.6(2)°. Selected bond lengths and bond angles of 3a are given in Table 3. The dihedral angle between the two planes defined by N12,Ti1,N32 and N42,Ti1,N50 is  $3.8(2)^{\circ}$ . Therefore, the ureato ligand lies essentially coplanar with the N12-Ti1-N32 fragment. A comparison of the bonding parameters of 2a and 3a with [PcTiO] 1 and [PcTiCl<sub>2</sub>]<sup>10</sup> is displayed in Table 4.

Table 3 Selected bond lengths [Å] and angles [°] for 3a

C41-N42	1.396(7)	N22–Ti	2.066(5)
C41–O41	1.221(7)	N32–Ti	2.104(5)
C41-N50	1.402(7)	N42–Ti	1.982(4)
N1–Ti	2.060(5)	N50-Ti	1.990(5)
N12–Ti	2.111(1)		
N42-Ti-N50	65.6(2)	N1-Ti-N12	82.0(2)
O41-C41-N42	130.6(5)	N1-Ti-N22	140.3(2)
N42-C41-N50	100.5(5)	C41-N42-Ti	97.1(3)
N22-Ti-N12	82.3(2)	C41-N50-Ti	96.5(3)
N1-Ti-N32	82.9(2)		
	. ,		

Table 4 Comparison of selected bond distances [Å] in [PcTiCl<sub>2</sub>], 1, 2a and **3a**.  $d(Ti-N_{isoindoline})$  refers to the average  $Ti-N_{isoindoline}$  distance

Complex	$d(Ti-N_{isoindoline})$	$d(Ti-N_{4-plane})$	Ref.
[PcTiCl <sub>2</sub> ]	2.087	0.84	10
2a 3a	2.062 2.085	0.60 0.76	This work This work



Fig. 6 Molecular structure of 3a, H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.

The molecular arrangement in the unit cell of 3a is displayed in Fig. 7. Two molecules of the solvent chlorobenzene are included. Similar to the structure of 2a, face-to-face dimers of the ureato titanium Pc's with a distance of 3.55(1) Å between two adjacent  $N_4$  planes are observed. The two molecules of the dimer are related to each other by an inversion centre.



Fig. 7 The molecular packing of **3a**. H atoms and two molecules of chlorobenzene are omitted for clarity.

### [PcTiO] catalyzed synthesis of carbodiimides

Carbodiimides are important class of compounds in organic chemistry because of their miscellaneous applications. They are used in esterification, synthesis of heterocyclic compounds or as coupling agents in the synthesis of peptides.<sup>37</sup> Diaryl- and dialkylcarbodiimides were catalytically synthesized for the first time in 1950 from isocyanates, using phospholanes or phosphalenes as a catalyst, in high purity and quantitative yield.<sup>38,39</sup> The methods used before this time led to lower yields and crude products.<sup>40,41</sup> Since then, other catalysts have been reported such as cyclic phosphoric acid amides, *e.g.* phosphatranes EP(MeNCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N (E = NMe, O, S)<sup>42</sup> or iminophosphoranes (Cl<sub>3</sub>P==NR)<sub>2</sub> (R =

 Table 5
 Attempted [PcTiO] catalyzed synthesis of carbodiimides (0.3 mol% catalyst, 6 d)

Product RNCNR	Yield (%)	Temp./°C	
R = Ph	78	170	
R = Tol	85	190	
R = 2,6-diisopropylphenyl	0	190	
R = cyclohexyl	10	170	

alkyl, aryl).<sup>43</sup> Transition metal imido complexes are well known as potential reagents for N–C bond formation reactions.<sup>44–46</sup>

During the study of the reaction of [PcTiO] **1** with excess arylisocyanates we found that upon six days of heating, a steady evolution of CO<sub>2</sub> and formation of a white precipitate of diarylcarbodiimides (RN=C=NR) occurs. We therefore investigated the catalytic properties of **1** in the formation of carbodiimides. Solvent-free heating of catalytic amounts of **1** (0.3 mol%) with cyclohexyl-, phenyl-, and *p*-tolylisocyanates in a temperature range of 170– 190 °C for about 6 days was found to yield the corresponding carbodiimides in high purity (Table 5). In the case of the aromatic isocyanates, a nearly quantitative yield was achieved. The products were isolated from the reaction mixture by vacuum distillation.

The reaction of 2,6-diisopropylphenylisocyanate with **1** does not lead to catalytic formation of the corresponding carbodiimide because of the steric hindrance mentioned above. After the addition of one equivalent of the isocyanate, the stable imido titanium Pc **2a** is formed and the catalytic cycle cannot be completed (Scheme 2). This catalytic system has a lot of advantages due to the catalyst's extreme chemical and thermal stability. Furthermore, the pure products can easily be isolated by distillation whereas the catalyst is retained as a residual blue mixture that is able to react with new reactants.

# Conclusion

The present work reveals that the reaction of [PcTiO] **1** with arylisocyanates depends largely on the size of the corresponding aryl group. For smaller groups, such as tolyl and mesityl, ureato complexes **3a** and **3b** were obtained. For the large 2,6-diisopropylphenyl group, imido complex **2a** was obtained. The X-ray crystal structures of **2a** and **3a** revealed the formation of face-to-face dimers in the solid state, which is also observed for other axially substituted phthalocyanines. Additionally, a more general synthetic route towards imido titanium compounds (**2b**-**c**) was developed. The metathetic reaction of **1** with isocyanates was successfully applied in the catalytic solvent-free formation of diaryl- and dialkylcarbodiimides.

# Experimental

All experiments and manipulations were carried out under a dry nitrogen atmosphere using standard Schlenk-tube or glovebox techniques. Solvents 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 2chloronaphthalene. Phenyl-, *p*-tolyl- and cyclohexylisocyanate were distilled under vacuum prior to use and kept in the dark under inert gas at -20 °C. [PcTiO] 1,<sup>9</sup> [Ti(NtBu)Cl<sub>2</sub>py<sub>3</sub>]<sup>27</sup>

Compound	2a	$3a \cdot 1.5C_6H_5Cl$
Empirical formula	C44H33N9Ti	C <sub>56</sub> H <sub>37.5</sub> Cl <sub>1.5</sub> N <sub>10</sub> OTi
Formula weight	735.69	967.53
Crystal system	Monoclinic	Triclinic
Space group	$P 2_1/n$	$P\overline{1}$
a/Å	10.9544(9)	12.3080(17)
b/Å	17.0865(9)	12.5821(14)
c/Å	19.5582(15)	16.717(2)
$\alpha / ^{\circ}$		70.981(10)
$\beta/^{\circ}$	104.458(6)	78.757(11)
$\gamma /^{\circ}$		68.628(10)
$V/Å^3$	3542.1(4)	2270.6(5)
Ζ	4	2
$\rho$ (calc.)/Mg m <sup>-3</sup>	1.379	1.415
$\mu/\text{mm}^{-1}$	0.289	0.332
$R_{\rm int}$	0.0926	0.1148
Reflns collected	3550	3220
Goodness-of-fit on $F^2$	0.866	0.924
$wR_2$ (all data)	0.0866	0.1321
$R_1$ (observed data)	0.0435	0.0678

and  $[Ti(NMes)Cl_2py_2]^{27}$  were prepared according to literature methods. PcH<sub>2</sub> was deprotonated with 2.5 eq. benzyl potassium in THF.

Electronic spectra were recorded on a Shimadzu UV-1601 PCspectrophotometer. IR spectra were recorded on a Bruker IFS 588 spectrometer or a Nicolet 510 M FT-IR- spectrometer. EI mass spectra were taken on CH7 Mass-spectrometer, Varian MAT. 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 the matrix or without a matrix. The reported m/z values refer to the highest peak of the isotopic pattern according to the natural abundance of the isotopes. Elemental analysis of C, H and N was carried out using an Elementar, Vario EL. Atom Absorption Spectrometry (AAS) for the determination of the titanium content was carried out using a Perkin Elmer Atom absorption spectrometer 5000. 1H-NMR spectra were recorded on Bruker AMX 500 or on Bruker AC 300. Thermal gravimetric analyses (TGA) were carried out using a TGA/SDTA 851, Mettler. The heating range was from 25 °C to 800 °C with a heating rate of 10 °C min<sup>-1</sup> and a slower rate of 1 °C min<sup>-1</sup> from 250 to 400 °C. Selected crystallographic data of 2a and 3a are given in Table 6 and complete data are given in the CIF file (Supporting Information<sup>†</sup>). Data were collected on an IPDS area detector system using graphite monochromated Mo-K $\alpha$  X-radiation ( $\lambda = 0.71073$  Å). The structures were solved by direct methods (programs SHELXS-9747 or SIR200248) and refined on  $F^2$  by full matrix least squares using SHELXL-97. 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. The asymmetric unit of 3a contains one molecule of chlorobenzene with occupancy 1 and one molecule of chlorobenzene with occupancy 0.5. The latter is disordered due to crystallographic inversion symmetry.

#### Syntheses

**[PcTi(NDip)] (2a).** A mixture of [PcTiO] (300 mg, 0.52 mmol) and 2,6-diisopropyl-phenylisocyanate (2 mL, 10.4 mmol, 20-fold excess) in 20 mL of chloronaphthalene was heated at 180 °C for

6 h. The color turned dark green. The produced CO<sub>2</sub>-gas was replaced by N<sub>2</sub> from time to time. After cooling, the product was precipitated by addition of 20 mL hexane. The precipitate was collected on a glass frit and purified by successive extractions with refluxing MeCN and toluene ( $10 \times 50$  mL each), and finally washed with pentane. The product **2a** was then dried at  $120 \text{ °C}/10^{-3}$  mbar for 3 h. Blue–violet needles of [PcTi(NDip)] **2a** were grown by controlled cooling of a chloronaphthalene solution from 180 °C to room temperature within 6 h. Beautiful crystals of **2a** could also be obtained by controlled cooling of the reaction mixture when the reaction was carried out in an excess (10 mL) of the isocyanate without solvent (see Table 6).

Yield: 320 mg (0.43 mmol; 83%) blue–violet crystals. Anal. calcd for C<sub>44</sub>H<sub>33</sub>N<sub>9</sub>Ti: C, 71.84; H, 4.52; N, 17.14; found: C, 71.81; H, 4.50; N, 16.19. UV/vis  $\lambda_{max}$ (CHCl<sub>3</sub>)/nm: 698.5 (s), 665.0 (sh), 628.0 (m), 344.0 (m). IR  $v_{max}$ (KBr)/cm<sup>-1</sup>: 2955 (w) [CH aliph.], 1607 (w), 1476 (m), 1457 (m), 1411 (m), 1330 (vs), 1284 (s), 1160 (m), 1117 (s), 1074 (s), 892 (m), 798 (w), 771 (m), 752 (m), 725 (vs). <sup>1</sup>H-NMR (500 MHz, C<sub>6</sub>D<sub>5</sub>Br, 373 K)  $\delta$  (ppm): 0.03 (d, *J* = 4.91 Hz, 12H, *Me*<sub>*i*Pr</sub>), 0.27–0.39 (m, 2H, *CHMe*<sub>2</sub>), 5.88–5.97 (m, 2H, *m*-H), 6.02–6.11 (m, 1H, *p*-H), 8.36–8.47 (m, 8H, *H*<sub>2,3Pe</sub>), 9.83–9.93 (m, 8H, *H*<sub>1,4Pe</sub>). MS (EI, *m/z*): 735 [M]<sup>+</sup>.

**[PcTi(NtBu)] (2b).** 500 mg (0.85 mmol) of PcK<sub>2</sub> were dissolved in 50 mL THF. A solution of 467 mg (1.10 mmol) [Ti(NtBu)Cl<sub>2</sub>py<sub>3</sub>] in 5 mL THF was added and the mixture was heated to 60 °C overnight. The violet product was collected by centrifugation and extracted with acetonitrile and toluene ( $3 \times 50$  mL each) and finally washed with pentane. The product was dried at 120 °C/10<sup>-3</sup> mbar.

Yield: 364 mg (68%) violet solid. Anal. calcd for  $C_{36}H_{25}N_9Ti$ : C, 69.47; H, 3.99; N, 19.96; found: C, 66.25; H, 3.69; N, 17.20: UV/vis  $\lambda_{max}$  (CH<sub>2</sub>Cl<sub>2</sub>)/nm: 690 (s), 657 (sh), 620 (sh), 348 (s). IR  $v_{max}$ (Nujol)/cm<sup>-1</sup>: 1330 (m), 1313 (s), 1284 (w), 1161 (w), 1116 (s), 1072(s), 893 (w), 868 (w), 778 (m), 750 (m). <sup>1</sup>H-NMR (300 MHz, THF- $d_8$ , 300 K)  $\delta$  (ppm): -1.45 (s, 9H, *Me*), 8.40 (m, 8H,  $H_{2,3Pc}$ ), 9.66 (m, 8H,  $H_{1,4Pc}$ )., MS (MALDI–TOF, *m*/*z*): 632 [M]<sup>+</sup>, 617 [M – Me]<sup>+</sup>, 575 [M – *t*Bu]<sup>+</sup>, 560 [M – (N*t*Bu)]<sup>+</sup>. (APCI–HRMS, *m*/*z*): 632.1787 [M<sup>+</sup>],  $C_{36}H_{25}N_9Ti$  requires 632.1785.

**[PcTi(NMes)] (2c).** 500 mg of (0.85 mmol) PcK<sub>2</sub> were dissolved in 50 mL THF. A solution of 542 mg (1.10 mmol) [Ti(NMes)Cl<sub>2</sub>py<sub>2</sub>] in 5 mL THF was added and the mixture was heated to 60 °C overnight. The violet product was collected by centrifugation and extracted with acetonitrile and toluene (3 × 50 mL each) and finally washed with pentane. The product was dried at 120 °C/10<sup>-3</sup> mbar.

Yield: 390 mg (66%) violet solid. Anal. calcd for C<sub>41</sub>H<sub>27</sub>N<sub>9</sub>Ti: C, 71.00; H, 3.92; N, 18.17; found: C, 63.60; H, 3.90; N, 18.00; UV/vis  $\lambda_{max}$  (CH<sub>2</sub> Cl<sub>2</sub>)/nm: 689 (s), 658 (sh), 622 (sh), 334 (s). IR  $\nu_{max}$ (KBr)/cm<sup>-1</sup>:1330 (s), 1313 (s), 1284 (m), 1161 (w), 1116 (s), 1072 (s), 1010 (m), 893 (w), 747 (m). <sup>1</sup>H-NMR (300 MHz, THF-*d*<sub>8</sub>)  $\delta$  (ppm): -0.3 (s, 6H, *o*-*Me*), 1.24 (s, 3H, *p*-*Me*), 5.31 (s, 2H, *m*-*H*), 8.42 (m, 8H, *H*<sub>2,3Pc</sub>), 9.69 (m, 8H, *H*<sub>1,4Pc</sub>), <sup>13</sup>C-NMR (100 MHz, THF-*d*<sub>8</sub>)  $\delta$  (ppm): 151.5, 139.1, 131.1, 129.1, 124.1, 121.5, 93.4 (*C*<sub>AT</sub>), 20.5 (*p*-*Me*), 17.7 (*o*-*Me*).

MS (MALDI–TOF, *m*/*z*): 693 [M]<sup>+</sup>, 560 [M – NMes]<sup>+</sup>, (APCI– HRMS, *m*/*z*): 694.1946 [M+H]<sup>+</sup>, C<sub>41</sub>H<sub>27</sub>N<sub>9</sub>Ti requires 694.1942.

[PcTi(N,N'-di-p-tolylureato)] (3a). A mixture of [PcTiO] (300 mg, 0.52 mmol) and p-tolylisocyanate (1.3 mL, 10.4 mmol,

20-fold excess) in 20 mL of chloronaphthalene was heated at 180 °C for 6 h. The color turned dark green. The produced  $CO_2$ -gas was replaced by  $N_2$  from time to time. After cooling, the product was precipitated by addition of 20 mL hexane. The precipitate was collected on a glass frit and purified by successive extractions with refluxing MeCN (10 × 50 mL) and toluene (10 × 50 mL), and finally washed with pentane. The product **3a** was then dried at 120 °C/10<sup>-3</sup> mbar for 3 h. The same product **3a** was obtained when the reaction was carried out in excess (10 ml) of *p*-tolylisocyanate without solvent. Dark blue prism shaped crystals suitable for the crystallographic structure determination of **3a** were obtained by controlled cooling of its solution in chlorobenzene from 130 °C to room temperature within 3 h (see Table 6).

Yield: 316 mg (76%) blue–green solid. Anal. calcd for  $C_{47}H_{30}N_{10}OTi$ : C, 70.68; H, 3.78; N, 17.54; Ti, 5.99; found: C, 70.56; H, 3.85; N, 17.36; Ti, 5.84. UV/vis  $\lambda_{max}$  (CHCl<sub>3</sub>)/nm: 698.5 (s), 665.5 (sh), 629.0 (m), 345.0 (m). IR  $v_{max}$ (KBr)/cm<sup>-1</sup>: 1683(m)[C=O], 1589 (m), 1503 (m), 1489 (m), 1414 (w), 1332 (vs), 1286 (m), 1160 (m), 1118 (vs), 1069 (vs), 970 (s), 894 (s), 775 (s), 751 (s), 729 (vs). <sup>1</sup>H-NMR (500 MHz, C<sub>6</sub>D<sub>5</sub>Br, 373 K)  $\delta$  (ppm): 1.99 (s, 6H, *p-Me*), 4.98 (d, 4H, *o-H*), 6.32–6.44 (d, 4H, *m-H*), 8.25–8.35 (m, 8H,  $H_{2,3Pc}$ ), 9.64–9.72 (m, 8H,  $H_{1,4Pc}$ ). MS (MALDI–TOF, *m/z*): 798 [M]<sup>+</sup>; 665 [M – RNCO]<sup>+</sup>.

**[PcTi(***N*,*N*'-dimesitylureato)] (3b). A mixture of [PcTiO] (300 mg, 0.52 mmol) and mesitylisocyanate (1.6 g, 10.4 mmol, 20-fold excess) in 20 mL of chloronaphthalene was heated at 180 °C for 6 h. The color turned dark green. The produced CO<sub>2</sub>-gas was replaced by N<sub>2</sub> from time to time. After cooling, the product was precipitated by addition of 20 mL hexane. The precipitate was collected on a glass frit and purified by successive extractions with refluxing MeCN (10 × 50 mL) and toluene (10 × 50 mL) and finally washed with pentane. The product **3b** was then dried at 120 °C/10<sup>-3</sup> mbar for 3 h.

Yield: 325 mg (73%) blue–green solid. Anal. calcd for  $C_{51}H_{38}N_{10}OTi$ : C, 71.66; H, 4.48; N, 16.39; Ti, 5.60; found: C, 71.24; H, 4.52; N, 16.26; Ti, 5.66. UV/vis  $\lambda_{max}$ (CHCl<sub>3</sub>)/nm: 700.5 (s), 627.5 (m), 343.0 (m). IR  $v_{max}$ (KBr)/cm<sup>-1</sup>: 1684 (s) [C==O], 1502 (w), 1469 (w), 1417 (w), 1333 (s), 1287 (w), 1259 (m), 1161 (w), 1117 (m), 1082 (w), 1069 (w), 1057 (m), 1005 (w), 894 (w), 829 (w), 749 (m), 734 (vs). <sup>1</sup>H-NMR (500 MHz, C<sub>6</sub>D<sub>5</sub>Br, 373 K)  $\delta$  (ppm): 0.77 (s, 12H, *o*-Me), 2.05 (s, 6H, *p*-Me), 6.30 (m, 4H, *m*-H), 8.28–8.36 (m, 8H,  $H_{2,3Pe}$ ), 9.67–9.73 (m, 8H,  $H_{1,4Pe}$ ). MS (MALDI–TOF, m/z): 855 [M]<sup>+</sup>, 693 [M – RNCO]<sup>+</sup>.

# Catalytic synthesis of carbodiimides from isocyanates using [PcTiO] as catalyst

General procedure for the catalytic carbodiimide synthesis. A mixture of the respective isocyanate and 0.3 mol% of [PcTiO] was refluxed at 170–190 °C for 6 days. The produced dark green suspension was distilled under reduced pressure and the obtained carbodiimide was collected as a colorless liquid or solid.

**Diphenylcarbodiimide.** 10.97 g phenylisocyanate (92.09 mmol) and 155.7 mg of [PcTiO] (0.27 mmol, 0.3 mol%).

Yield: 6.99 g (78%, colorless liquid). Bp. 158 °C (4.6 mbar). IR  $v_{\text{max}}(\text{Nujol})/\text{cm}^{-1}$ : 2110, 2139 [N=C=N]. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, 300 K)  $\delta$  (ppm): 7.42 (t, 4H, *m*-H), 7.24–7.31 (m, 6H,

*o*/*p*-*H*). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>, 300 K) δ (ppm): 138.4 (N=*C*=N), 135.2, 129.4, 125.5, 124.1. MS (EI, *m*/*z*): 194 [M]<sup>+</sup>.

**Di**(*p*-tolyl)carbodiimide. 10.97 g *p*-tolylisocyanate (79.39 mmol) and 139.4 mg of [PcTiO] (0.24 mmol, 0.3 mol%).

Yield: 7.47 g (85%, colorless liquid) Bp. 173 °C (3.9 mbar). IR  $v_{max}$ (Nujol)/cm<sup>-1</sup>: 2110, 2139 [N=C=N]. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, 300 K)  $\delta$  (ppm): 6.97–7.04 (m, 8H,  $H_{Ar}$ ), 2.23 (s, 6H, *Me*). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>, 300 K)  $\delta$  (ppm): 135.9 (N=C=N), 135.8, 135.2, 130.0, 123.8, 20.0. MS (EI, *m/z*): 222 [M]<sup>+</sup>.

**Dicyclohexylcarbodiimide.** 9.88 g cyclohexylisocyanate (78.93 mmol) and 132.8 mg of [PcTiO] (0.23 mmol, 0.3 mol%). Distillation of this suspension under reduced pressure afforded two fractions, the first being the unreacted cyclohexylisocyanate (7.86 g), and the second dicyclohexylcarbodiimide.

Yield: 0.83 g (10%, white solid.). Bp. 112 °C (4.7 mbar). IR  $v_{max}(Nujol)/cm^{-1}$ : 2122 [N=C=N]. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, 300 K)  $\delta$  (ppm): 2.96 (sept, 2H, *ipso-H*), 0.95–1.71 (m, 20H, CH<sub>2</sub>). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>, 300 K)  $\delta$  (ppm) 138.9 (N=C=N), 55.1, 34.4, 25.0, 24.2. MS (EI, *m/z*): 206 [M]<sup>+</sup>.

**Bis(2,6-diisopropylphenyl)carbodiimide.** 2.37 g 2,6-diisopropylphenylisocyanate (11.66 mmol) and 20.2 mg of [PcTiO] (0.035 mmol, 0.3 mol%) were refluxed at 190 °C for 6 days under inert gas atmosphere. A faint green suspension was produced. Distillation of this suspension under reduced pressure afforded only the starting material.

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