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Axial Functionalization of Sterically Hindered Titanium Phthalocyanines

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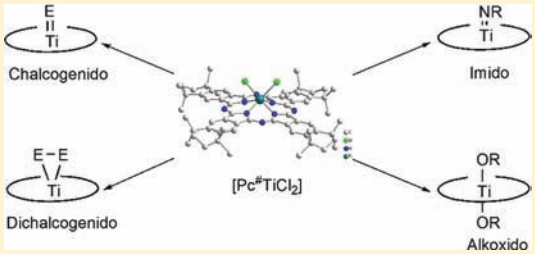
Supporting Information

ABSTRACT: Several axially functionalized, weakly aggregating titanium phthalocyanines (Pc) have been synthesized and characterized. Soluble titanium dichlorido tetrakis-(1,1,4,4-tetramethyl-6,7-tetralino)-porphyrazine [Pc#TiCl$_2$] (**5**) has been prepared by reductive cyclotetramerization of the respective dinitrile precursor in the presence of TiCl$_4$. **5** and the analogous oxido compound [Pc#TiO] (**1**) are versatile starting materials for the formation of other axially functionalized titanium phthalocyanines such as organoimido (**6**, **7**), alkoxido and aryloxido (**8**, **9**), peroxido (**10**), sulfido (**12**), disulfido (**11**), selenido (**14**) or diselenido (**13**) species. Furthermore the deprotonated ligand salts [Pc#M$_2$] (M = Li (**2**), Na (**3**), K (**4**) are described. The reactivity of the titanium compounds was studied in atom group transfer reactions and ethene polymerization. The crystal structures of **5** and the free ligand Pc#H$_2$ are reported. **5** crystallizes from dichloromethane in the cubic space group $Im\bar{3}$. The two chlorido ligands exhibit a cis arrangement. The free ligand Pc#H$_2$ crystallizes in the trigonal space group $R\bar{3}$.



INTRODUCTION

Phthalocyanine complexes [PcM] are an important class of red/near-IR (Q-band) absorbing chromophores used as dyes and semiconductors in optoelectronic materials.[1−4] They find application in devices such as organic field effect transistors (OFETs)[5] or as sensitizers for wide band gap oxide semiconductors in organic heterojunction dye sensitized solar cells (DSSCs).[6] The solar conversion efficiencies of [PcM] appear to be dependent on the metal,[7] on the Pc polarizability,[8] on the degree of unfavorable Pc aggregation, and on the lack of directionality of the excited state.[9] To reduce the aggregation and enhance the solubility, randomly tetra-*tert*-butyl substituted Pcs, [Pc^{tBu}Zn] or [Pc^{tBu}TiO], are commonly employed. This material is a mixture of regio isomers, which leads to poorly resolved NMR spectra and prevents the molecules from forming ordered or even single crystalline phases. In the case of the parent, ring-unsubstituted metal phthalocyanines, the reactivity patterns have been much less studied than those of related porphyrins and other N$_4$-macrocycle supported complexes because of the insolubility of [PcM]. The group of Woo, for example, has developed a variety of synthetic strategies leading to titanium porphyrins bearing imido, amido, alkoxo,[10] hydrazido,[11] and chalcogenido[12] functionalities as well as subvalent Ti(II) porphyrins.[13−15] Titanium peroxido porphyrins have also been described.[16] Similarly, the group of Mountford synthesized a variety of axially substituted titanium complexes coordinated by tetraaza macrocyclic ligands.[17−21]

Until recently, the chemistry of titanium phthalocyanines was mainly focused on variations of the equatorial Pc ligand system.[22−27] The axial functionality can be determined by the metal template used in the reductive cyclotetramerization. Typically, this method affords titanyl phthalocyanines [Pc^{R}TiO], and relatively few synthetic protocols yielding titanium chlorido or dichlorido phthalocyanines have been described in the literature.[28,29] The exchange of an axial ligand in the macrocyclic complex was mostly described for soluble titanyl phthalocyanines. Next to the parent titanyl phthalocyanines, other axially substituted PcTis reported in the literature are chlorido,[30] oxalato, catecholato, and dithiocatecholato derivatives.[23,31,32] Catecholates have been used as axial ligands to build phthalocyanine dimers and oligomers which are useful for the recognition of chiral catechols.[33−36] [PcTi(S$_2$)] has been synthesized and characterized by X-ray diffraction,[37] and sulfido and selenido complexes have been mentioned in a patent, but not characterized.[38] Recently, we have reported the synthesis of titanium imido and ureato phthalocyanines starting from the titanyl complexes or the deprotonated Pc ligand.[37,39] The large variety of transformations feasible for porphyrins and other macrocyclic complexes has not yet been fully transferred to phthalocyanine chemistry. To expand our studies on soluble, isomerically pure, alkyl substituted phthalocyanines, we synthesized [Pc#TiO] **1** (Figure 1).[40] In this work we describe the synthesis of titanium Pc# derivatives bearing different substituents in the axial positions.

EXPERIMENTAL SECTION

General Procedures. 6,7-Dicyano-1,1,4,4-tetramethyltetraline was prepared according to literature procedures[41,42] and purified by

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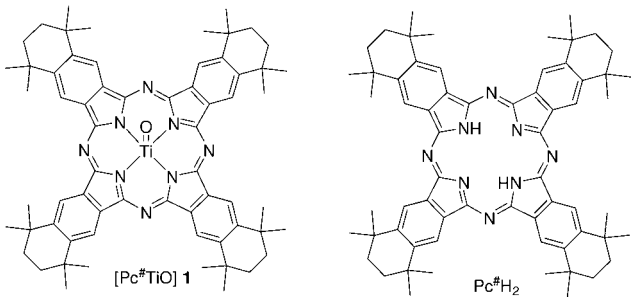

Figure 1. [Pc#TiO] **1** and the free ligand $Pc^{\#}H_2$.

column chromatography (silica gel, CH_2Cl_2) prior to use. Chloronaphthalene was obtained from Acros as a mixture of 1-chloronaphthalene (90%) and 2-chloronaphthalene (10%). Solvents were dried according to standard methods and stored under inert gas over molecular sieves. $TiCl_4$ and $Ti(OnBu)_4$ were obtained from Acros and stored under inert gas. Preparations were carried out under dry argon atmosphere using standard Schlenk or glovebox techniques.

The electronic spectra were recorded on an Avantes AvaSpec-2048 spectrometer in a glovebox. IR spectra were recorded on a Bruker Alpha FT-IR spectrometer with an ATR measurement setup (diamond cell) in a glovebox using neat samples. APCI mass spectra were taken on a Finnigan LTQ-FT spectrometer using dichloromethane as solvent. MALDI−TOF mass spectra were taken on a Bruker Biflex III using pyrene as matrix. Elemental analyses of C, H, N, and S were carried out using an Elementar vario MICRO cube. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 or Bruker DRX 400.

X-ray diffraction (XRD) analyses were performed on a Stoe IPDS 2 area detector system using Mo K_α radiation (λ = 71.073 pm) at 100 K. Stoe IPDS software[43] was used for integration and data reduction; structure solution and refinement was done with the WinGX program[44] suite using SIR2004[45] and SHELX-97.[46] Molecular graphics were produced with Diamond 3.2 g.[47]

In two cases, heavily disordered dichloromethane molecules could not be modeled adequately. The SQUEEZE routine of the PLATON program package[48] was used in these cases to remove the corresponding delocalized electron density from the data sets.

$Pc^{\#}H_2$. This compound was prepared by a modification of the method described by Mikhalenko et al.:[42] 176 mg of lithium (25 mmol, 5.0 equiv) were dissolved in 10 mL of 1-octanol. To complete the dissolution the suspension was stirred at 60 °C for 30 min. After cooling 1.2 g of 6,7-dicyano-1,1,4,4-tetramethyltetraline (5 mmol, 1.0 equiv) were added, and the mixture was stirred at 130 °C for 24 h. The dark blue mixture was cooled, and the product was precipitated by adding 60 mL of methanol and 1 mL of 85% H_3PO_4. The turquoise solid was filtered off and extracted with 3 × 60 mL of hot methanol, washed with diethylether, and dried under vacuum. Suitable crystals for X-ray diffraction were obtained from a saturated, degassed toluene solution layered with pentane in the dark. Yield: 733 mg, 0.77 mmol, 73%. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.48 (s, 8H), 2.06 (s, 16H), 1.81 (s, 48H), −0.03 (s, 2H, N-*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.4, 134.7, 121.3, 36.1, 35.6, 33.0 (not all quaternary carbon atoms were detected). IR: υ = 2956 (s), 2920 (s), 2853 (s), 1619 (m), 1575 (m), 1455 (s), 1360 (m), 1303 (m), 1258 (m), 1184 (w), 1072 (m), 1006 (s), 946 (m), 845 (m), 753 (s) cm^{-1}. UV−vis (CH_2Cl_2): λ = 710 (s), 676 (s), 650 (sh), 342 (s) nm. MS (APCI-HR(+)): m/z = 955.6115 $[M+H]^+$, $C_{64}H_{75}N_8$ requires 955.6109.

[$Pc^{\#}Li_2$] (2). Fifty milligrams of $Pc^{\#}H_2$ (0.05 mmol, 1.0 equiv) and 40 mg of LiHMDS (0.24 mmol, 4.8 equiv) were stirred overnight in 3 mL of tetrahydrofuran (THF) at 60 °C. A blue solid was separated, washed with pentane, and dried under vacuum. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.29 (s, 8H), 2.03 (s, 16H), 1.86 (s, 48H) ppm. UV−vis (CH_2Cl_2): λ = 680 (s), 611 (sh), 343 (m) nm. MS (MALDI-TOF(+)): m/z = 967.8 $[M]^+$, 961.7 $[Pc^{\#}HLi]$. According to NMR spectroscopy and mass spectrometry, a mixture of **2**, $Pc^{\#}HLi$ and $Pc^{\#}H_2$ was obtained.

[$Pc^{\#}Na_2$] (3). Fifty milligrams of $Pc^{\#}H_2$ (0.05 mmol, 1.0 equiv) and 48 mg of NaHMDS (0.26 mmol, 5.0 equiv) in 5 mL of THF were heated to 60 °C overnight. Volatiles were removed under reduced pressure, and the resulting bluegreen solid was washed with toluene and pentane. ^1H NMR (300 MHz, $CDCl_3$ + 1 drop THF-d_8): δ = 9.11 (s, 8H), 1.98 (s, 16H), 1.74 (s, 48H) ppm. UV−vis (CH_2Cl_2): λ = 683 (s), 619 (sh), 340 (m) nm. MS (MALDI-TOF(+)): m/z = 1000.2 $[M]^+$.

[$Pc^{\#}K_2$] (4). Seventy milligrams of $Pc^{\#}H_2$ (0.07 mmol, 1.0 equiv) were suspended in 8 mL of THF and cooled to 0 °C. A solution of 24 mg of KBn (0.18 mmol, 2.5 equiv) in 1 mL of THF was added dropwise. The mixture was stirred for 3 h and warmed to room temperature. After filtration over Celite the volatiles were removed under reduced pressure. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.31 (s, 8H), 2.02 (s, 16H), 1.77 (s, 48H) ppm. UV−vis (CH_2Cl_2): λ = 681 (s), 616 (sh), 345 (m), 252 (s) nm. MS (MALDI-TOF(+)): m/z = 1033.2 $[M]^+$. According to NMR spectroscopy, a mixture of **3** and $Pc^{\#}H_2$ was obtained.

***cis*-[$Pc^{\#}TiCl_2$] (5).** A 1.00 g portion of 6,7-dicyano-1,1,4,4-tetramethyl-tetraline (4.20 mmol, 4.4 equiv) and 179 mg of $TiCl_4$ (0.95 mmol, 1.0 equiv) in 6 mL of 1-chloronaphthalene were placed in an oil bath preheated to 160 °C and stirred overnight. After 1 h an intensely geen mixture was obtained. After cooling the product was precipitated by addition of 40 mL of hexane. The violet microcrystalline solid was collected by centrifugation, extracted with 3 × 40 mL of THF, washed with pentane, and dried under vacuum. Suitable crystals for X-ray diffraction were obtained from a saturated CH_2Cl_2 solution at 4 °C. Yield: 512 mg of violet microcrystals, 0.48 mmol, 50%. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.67 (s, 8H), 2.08 (s, 16H), 1.88 (s, 24H), 1.81 (s, 24H) ppm. IR: υ = 2956 (s), 2922 (s), 2859 (s), 1615 (w), 1492 (m), 1455 (m), 1431 (m), 1385 (w), 1305 (s), 1257 (m), 1187 (w), 1087 (s), 1066 (s), 974 (m), 868 (m), 789 (s), 706 (m) cm^{-1}. UV−vis (CH_2Cl_2): λ = 713 (s), 640 (sh), 348 (m), 235 (s) nm. MS (APCI-HR(+)): m/z = 1031.5543 $[M\text{-}2Cl+OMe]^+$, $C_{65}H_{75}N_8OTi$ requires 1031.5541 (methanolysis occurs upon ionization in the presence of methanol).

[$Pc^{\#}Ti(NtBu)$] (6). Seven milligrams of *tert*-butylamine (0.10 mmol, 2.1 equiv) in 5 mL of toluene were deprotonated with 0.06 mL of a 1.6 M *n*-BuLi solution in hexane (0.10 mmol, 2.1 equiv). This mixture was added dropwise to a suspension of 50 mg of **5** (0.05 mmol, 1.0 equiv) in 5 mL of toluene. It was stirred overnight at room temperature, and a green solution and a white precipitate were obtained. After filtration over Celite the volatiles were removed under reduced pressure. The resulting green solid was dried under vacuum. Yield: 10 mg green powder, 0.01 mmol, 21%. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.55 (s, 8H), 2.07 (s, 16H), 1.88 (s, 24H), 1.78 (s, 24H), −1.36 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.2, 148.3, 120.8, 35.1, 34.3, 32.0, 31.8 ppm (not all quaternary carbon atoms were detected). IR: υ = 2957 (m), 2920 (m), 2858 (m), 1614 (w), 1454 (m), 1308 (s), 1011 (s), 765 (m), 684 (m), 454 (w) cm^{-1}. UV−vis (CH_2Cl_2): λ = 710 (s), 645 (sh), 344 (m), 240 (s) nm. MS (MALDI-TOF(+)): m/z = 1073.5 $[M]^+$, 1058.6 $[M\text{-}Me]^+$, 1018.5 $[M\text{-}tBu]^+$, 1002.4 $[M\text{-}NtBu]^+$. MS (APCI-HR(+)): m/z = 1072.6183 $[M+H]^+$, $C_{68}H_{82}N_9Ti$ requires 1072.6167.

[$Pc^{\#}Ti(NMes)$] (7). Sixty-five milligrams of mesitylamine (0.48 mmol, 2.1 equiv) in a mixture of 5 mL of toluene and 0.5 mL of THF were deprotonated with 0.3 mL of a 1.6 M *n*-BuLi solution in hexane (0.48 mmol, 2.1 equiv). The suspension was added dropwise to 250 mg of **5** (0.23 mmol, 1.0 equiv) in 20 mL of toluene. The mixture was stirred overnight at room temperature yielding a green solution and a white precipitate. The mixture was filtered over Celite, washed with THF, and the filtrate was evaporated to dryness. The blue solid was washed with acetonitrile and pentane and dried under vacuum. Yield: 198 mg blue solid, 0.18 mmol, 75%. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.55 (s, 8H), 5.44 (s, 2H), 2.07 (s, 16H), 1.88 (s, 24H), 1.79 (s, 24H), 1.45, (s, 3H), −0.18 (s, 6H) ppm. ^1H NMR (300 MHz, C_6D_6): δ = 10.03 (s, 8H), 5.30 (s, 2H), 1.78 (s, 16H), 1.56 (s, 24H), 1.52 (s, 24H), 1.28, (s, 3H), 0.11 (s, 6H) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 152.4, 149.1, 136.5, 132.3, 129.3, 126.6, 122.3, 35.9, 35.7, 32.7, 32.6, 20.2, 16.9 ppm (not all quaternary carbon atoms were detected). IR: υ

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= 2956 (m), 2921 (m), 2857 (m), 1467 (m), 1306 (s), 1187 (m), 1068 (s), 850 (m), 707 (m), 543 (w) cm^{-1}. UV−vis (CH_2Cl_2): λ = 710 (s), 640 (sh), 343 (s), 238 (s) nm. MS (APCI-HR(+)): m/z = 1134.6300 $[M+H]^+$, $C_{73}H_{84}N_9Ti$ requires 1134.6324.

***trans*-[Pc#Ti(O*t*Bu)$_2$] (8).** Fifty milligrams of **5** (0.05 mmol, 1.0 equiv) and 11 mg of KO*t*Bu (0.10 mmol, 2.1 equiv) were stirred at room temperature in a mixture of 3 mL of toluene and 1 mL of THF for 3 h. The mixture was filtered over Celite, washed with THF, and the filtrate was evaporated to dryness. The green solid was washed with hexane and dried under vacuum. Yield: 9 mg green powder, 0.01 mmol, 17%. ^{1}H NMR (300 MHz, C_6D_6): δ = 10.01 (s, 8H), 1.75 (s, 16H), 1.50 (s, 48H), −1.91 (s, 18H) ppm. IR: υ = 2958 (s), 2922 (s), 2859 (s), 1616 (w), 1471 (m), 1319 (s), 1305 (s), 1216 (w), 1183 (m), 1063 (s), 999 (s), 871 (m), 859 (s), 789 (m), 707 (m), 567 (m) cm^{-1}. UV−vis (CH_2Cl_2): λ = 712 (s), 639 (sh), 340 (s) nm. MS (APCI-HR(+)): m/z = 1147.6754 $[M+H]^+$, $C_{72}H_{90}N_8O_2Ti$ requires: 1147.6748.

***cis*-[Pc#Ti(OMes)$_2$] (9).** Fifty milligrams of **5** (0.05 mmol, 1.0 equiv) and 11 mg of LiOMes (0.10 mmol, 2.1 equiv) were suspended in a mixture of 3 mL of toluene and 1 mL of THF and stirred at 50 °C overnight. The mixture was filtered over Celite, washed with THF, and the volatiles were removed under reduced pressure. The blue solid was washed with hexane and dried under vacuum. Yield: 20 mg green powder, 0.02 mmol, 34%. ^{1}H NMR (300 MHz, C_6D_6): δ = 9.92 (s, 8H), 5.46 (s, 4H), 1.76 (s, 16H), 1.56 (s, 24H), 1.49 (s, 24H), 1.37 (s, 6H), 0.38 (s, 12H) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 154.2, 149.2, 135.3, 130.8, 129.5, 129.1, 123.2, 122.9, 122.0, 36.0, 35.6, 32.8, 32.7, 20.5, 15.8 ppm. IR: υ = 2956 (s), 2921 (s), 2858 (s), 1615 (w), 1456 (s), 1432 (m), 1363 (w), 1305 (s), 1239 (m), 1187 (m), 1066 (s), 1022 (s), 986 (m), 896 (m), 859 (s), 759 (m), 664 (m), 546 (m) cm^{-1}. UV−vis (CH_2Cl_2): λ = 717 (s), 643 (sh), 337 (s) nm. MS (APCI-HR(+)): m/z = 1031.5543 $[M\text{-}2OMes+OMe]^+$, $C_{65}H_{75}N_8OTi$ requires: 1031.5541 (methanolysis occurs upon ionization in the presence of methanol).

[Pc#Ti(O$_2$)] (10). During the preparation and workup light was kept from the product by wrapping all flasks in aluminum foil. Fifty milligrams of [Pc#TiO] **1**[40] (0.05 mmol, 1.0 equiv) in 10 mL of dichloromethane and 9 μL of H_2O_2 (30% in water, 0.07 mmol, 1.5 equiv) were vigorously stirred for 2 h. The mixture was extracted with water until no more peroxide could be detected (KI_{aq}). The organic layer was dried over $MgSO_4$, filtered, and the solvent was evaporated. Yield: 12 mg green powder, 0.01 mmol, 24%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.58 (s, 8H), 2.07 (s, 16H), 1.86 (s, 24H), 1.80 (s, 24H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.2, 149.6, 134.3, 122.3, 35.3, 34.4, 31.8, 31.7 ppm. IR: υ = 2959 (m), 2922 (m), 2860 (m), 1616 (w), 1499 (m), 1456 (m), 1433 (w), 1386 (w), 1306 (s), 1260 (m), 1188 (m), 1090 (s), 1071 (s), 1018 (s), 895 (m, ν_{O-O}), 867 (m), 792 (s), 707 (m), 642 (w, $\nu_{Ti-O\ sym}$), 609 (m, $\nu_{Ti-O\ asym}$) cm^{-1}. UV−vis (CH_2Cl_2): λ = 714 (s), 644 (sh), 348 (m), 281 (s) nm. MS (APCI-HR (+)): m/z = 1017.5376 $[M\text{-}O+H]^+$, $C_{64}H_{73}N_8OTi$ requires 1017.5387. MS (MALDI-TOF(+)): m/z = 1035.1 $[M]^+$.

[Pc#Ti(S$_2$)] (11). Fifty milligrams of **5** (0.05 mmol, 1.0 equiv), 31 mg of C_8K (0.23 mmol, 5.0 equiv), and 12 mg of S_8 (0.05 mmol, 1.0 equiv) in 20 mL of THF were stirred overnight at room temperature. The resulting green solution was filtered over Celite, evaporated to dryness, and washed with hexane. Yield: 20 mg green solid, 0.02 mmol, 40%. To remove traces of elemental sulfur and obtain analytically pure **11**, the product was taken up in dichloromethane and filtered over a short silica column. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.54 (s, 8H), 2.06 (s, 16H), 1.85 (s, 24H), 1.79 (s, 24H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.5, 149.6, 134.2, 121.8, 36.1, 35.3, 33.0, 32.8 ppm. IR: υ = 2950 (m), 2926 (m), 2860 (m), 1616 (w), 1454 (m), 1307 (s), 1186 (m), 1067 (s), 1021 (m), 987 (m), 897 (m), 755 (m), 664 (m), 553 (m) cm^{-1}. UV−vis (CH_2Cl_2): λ = 717 (s), 648 (sh), 343 (s), 295 (s) nm. MS (APCI-HR(+)): m/z = 1065.4855 $[M+H]^+$, $C_{64}H_{73}N_8S_2Ti$ requires 1065.4880.

[Pc#TiS] (12). Twenty milligrams of **11** (0.02 mmol, 1.0 equiv) and 20 mg of PPh_3 (0.08 mmol, 4.0 equiv) were dissolved in 1 mL of $CDCl_3$ at room temperature. The immediate formation of [Pc#TiS] and Ph_3PS ($\delta(^{31}P)$ = 42.5 ppm) was monitored via ^{1}H, ^{31}P NMR and UV−vis spectroscopy. Volatiles were removed, and the green solid was extracted with 3 × 10 mL of hexane, 2 × 10 mL of acetonitrile, and dried under vacuum. Yield: 8 mg green solid, 0.01 mmol, 41%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.66 (s, 8H), 2.07 (s, 16H), 1.88 (s, 24H), 1.81 (s, 24H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.9, 149.6, 134.7, 122.0, 36.2, 35.4, 33.0, 32.9 ppm. IR: υ = 2959 (m), 2923 (m), 2861 (m), 1617 (w), 1457 (m), 1307 (s), 1188 (m), 1068 (s), 1022 (m), 870 (m), 753 (w), 664 (m), 572 (w), 450 (w) cm^{-1}. UV−vis (CH_2Cl_2): λ = 726 (s), 651 (sh), 360 (s), 300 (s), 256 (s) nm. MS (APCI-HR(+)): m/z = 1033.5133 $[M+H]^+$, $C_{64}H_{73}N_8STi$ requires 1033.5160.

[Pc#Ti(Se$_2$)] (13). Fifty milligrams of **5** (0.05 mmol, 1.0 equiv), 31 mg of C_8K (0.23 mmol, 5.0 equiv), and 29 mg of Se_8 (0.05 mmol, 1.0 equiv) in 20 mL of THF were stirred overnight at room temperature. The resulting green solution was filtered, evaporated to dryness and taken up in CH_2Cl_2. The mixture was filtered over silica to remove residual Se_8, evaporated, washed with hexane, and dried under vacuum. Yield: 18 mg green solid, 0.02 mmol, 33%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.52 (s, 8H), 2.06 (s, 16H), 1.85 (s, 24H), 1.78 (s, 24H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.1, 149.4, 134.3, 121.6, 36.1, 35.3, 33.0. 32.8 ppm. IR: υ = 2952 (m), 2923 (m), 2859 (m), 1454 (m), 1305 (s), 1186 (w), 1067 (s), 1021 (m), 897 (m), 865 (m), 751 (w), 706 (w), 543 (w) cm^{-1}. UV−vis (CH_2Cl_2): λ = 716 (s), 648 (sh), 354 (s), 290 (s), 242 (s) nm. MS (APCI-HR(+)): m/z = 1161.3771 $[M+H]^+$, $C_{64}H_{73}N_8Se_2Ti$ requires 1161.3781.

[Pc#TiSe] (14). Fifty milligrams of **13** (0.04 mmol, 1.0 equiv) and 20 mg of PPh_3 (0.08 mmol, 1.8 equiv) in 15 mL of CH_2Cl_2 were stirred for 1 h at room temperature. The immediate formation of [Pc#TiSe] and Ph_3PSe ($\delta(^{31}P)$ = 35.2 ppm) was monitored via ^{1}H, ^{31}P NMR, and UV−vis spectroscopy. Volatiles were removed, and the green solid was extracted with 2 × 20 mL of acetonitrile, 3 × 20 mL of hexane, and dried under vacuum. Yield: 39 mg green solid, 0.03 mmol, 84%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.67 (s, 8H), 2.09 (s, 16H), 1.91 (s, 24H), 1.84 (s, 24H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 152.0, 149.7, 134.7, 122.1, 36.2, 35.4, 33.0, 32.9 ppm. IR: υ = 2957 (m), 2922 (m), 2858 (m), 1616 (w), 1455 (w), 1306 (m), 1258 (s), 1187 (w), 1063 (s), 1015 (2), 897 (w), 868 (m), 792 (s), 706 (w), 543 (w) cm^{-1}. UV−vis (CH_2Cl_2): λ = 732 (s), 658 (sh), 371 (s), 334 (s), 256 (s) nm. MS (APCI-HR(+)): m/z = 1081.4611 $[M+H]^+$, $C_{64}H_{73}N_8SeTi$ requires 1081.4597.

[Pc#TiO→(Al(*i*Bu)$_3$)] (15). *Method a.* Sixty-five milligrams of **1** (0.06 mmol, 1.0 equiv) were dissolved in 10 mL of toluene. 0.38 mL (0.12 mmol, 2.0 equiv) of a 10% solution of $(iBu)_2AlOAl(iBu)_2$ in toluene were added at room temperature. After 2 h the volatiles were removed, and the blue solid was washed with hexane.

Method b. Fifty milligrams of **1** (0.05 mmol, 1.0 equiv) were dissolved in 10 mL of toluene. 0.07 mL (0.05 mmol, 1.0 equiv) of a 0.15 g/mL solution of Al(*i*Bu)$_3$ in toluene were added at room temperature. After 2 h the volatiles were removed, and the blue solid was washed with hexane.

^{1}H NMR (300 MHz, C_6D_6): δ = 10.06 (s, 8H), 1.75 (s, 16H), 1.53 (s, 24H), 1.50 (s, 24H), 0.50 (m, 3H), 0.16 (d, $^3J_{HH}$ = 6.41 Hz, 18H), −1.59 (d, $^3J_{HH}$ = 7.04 Hz, 6H) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 152.8, 150.9, 135.0, 123.1, 36.2, 35.5, 32.6, 32.6 (Pc#), 28.0, 26.4, 23.8 (Al*i*Bu$_3$) ppm. IR: υ = 2928 (m), 2856 (m), 1618 (w), 1456 (m), 1434 (m), 1306 (s), 1187 (m), 1088 (m), 1059 (s), 985 (w), 932 (m), 867 (m), 750 (m), 663 (m), 496 (w) cm^{-1}. UV−vis (toluene): λ = 733 (s), 660 (sh), 359 (s), 285 (s) nm.

Polymerization of Ethene. Ten μmol of the precatalyst (**1**, **5** or Eurecen 5031) were activated with 1000 equiv of MAO in 5 mL of chlorobenzene. Ethene was bubbled through 45 mL of chlorobenzene at 50 °C for 15 min. The solution of the activated precatalyst was added quickly, and the mixture was stirred under continuing ethene flow at 50 °C for 1 h. The mixture was quenched with HCl (1% in MeOH) and poured into 200 mL of methanol. The precipitated polymer was filtered, washed with methanol, dichloromethane, and ether and dried under vacuum at 60 °C.

Reactivity of 7 toward *p*-Cl-benzaldehyde. An NMR tube was charged with 10 mg of **7** (8.8 μmol, 1.0 equiv), 1.2 mg of *p*-Cl-

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benzaldehyde (8.8 μmol, 1.0 equiv), and 0.6 mL of C_6D_6. The reaction progress was monitored via ^{1}H NMR spectroscopy. After 24 h at room temperature, a **7**:**1** ratio of 70%:30% was determined by integration of the aromatic Pc# protons. Unambiguous assignment of resonances of *p*-chlorobenzylidene mesitylamine was not possible because of the presence of different species. MS (ESI-HRMS(+)): m/z = 258.1050 [*p*-chlorobenzylidene mesitylamine+H]$^+$. $C_{16}H_{17}ClN$ requires 258.1044.

Reactivity of 7 toward Nitrosobenzene. An NMR tube was charged with 20 mg of **7** (17.6 μmol, 1.0 equiv), 1.9 mg of nitrosobenzene (17.6 μmol, 1.0 equiv), and 0.6 mL of C_6D_6. The reaction progress was monitored via ^{1}H NMR spectroscopy. After 5 min at room temperature, all starting material was consumed, and **1** and mesityl phenyl diazene were formed. ^{1}H NMR (300 MHz, C_6D_6): δ = 7.58 (m, 1H), 6.96−6.79 (m, 4H), 6.48 (s, 2H), 2.20 (s, 3H), 1.86 (s, 6H) ppm. MS (ESI-HR(+)): m/z = 225.1388 [mesityl phenyl diazene+H]$^+$. $C_{15}H_{17}N_2$ requires 225.1386.

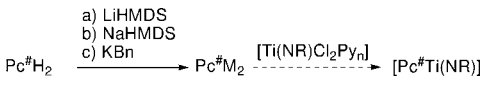
Reactivity of 7 toward Styrene Oxide. An NMR tube was charged with 17 mg of **7** (15.8 μmol, 1.0 equiv), 1.7 μL of styrene oxide (15.8 μmol, 1.0 equiv), and 0.6 mL of C_6D_6. No conversion was observed after 24 h.

Reactivity of 7 toward Triphenylphosphine Oxide. An NMR tube was charged with 20 mg of **7** (17.6 μmol, 1.0 equiv), 5 mg of Ph_3PO (17.6 μmol, 1.0 equiv), and 0.6 mL of C_6D_6. No conversion was observed after 24 h.

RESULTS AND DISCUSSION

Preparation. *Organoimido, Alkoido, and Aryloxido Complexes.* Axially functionalized titanium phthalocyanines could be prepared by reaction of PcK_2 with titanium imido precursors or by reaction of [PcTiO] with aryl isocyanates.[39] However, the reactions of different alkali metal salts **2**−**4** of the soluble ligand Pc#H$_2$ with titanium imido precursors were unselective (Scheme 1). Pc#Na$_2$ did not react with [Ti(NR)-

Scheme 1. Preparation of Titanium Imido Compounds Starting from Pc#H$_2$



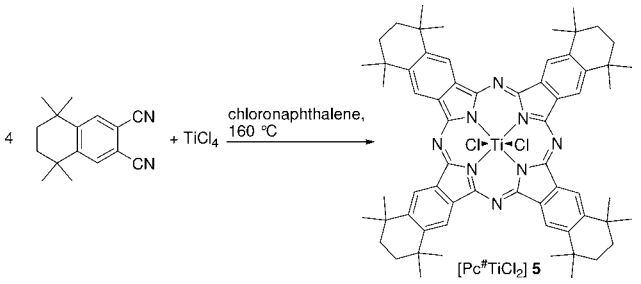
Cl_2Py_n] (n = 2, 3). For Pc#Li$_2$ and Pc#K$_2$, the resulting imido compounds [Pc#Ti(NR)] were contaminated with the free ligand Pc#H$_2$ which resulted from incomplete deprotonation. These mixtures could not be separated by extraction or recrystallization because of their similar solubilities.

For the soluble [Pc#TiO], metathesis with aryl isocyanates at high temperatures gave mixtures of [Pc#TiO], imido compounds [Pc#Ti(NAr)], and ureato compounds [Pc#Ti(ArN-(CO)N′Ar)]. Because of their hydrolytic sensitivity these mixtures could not be separated by column chromatography.[49] Thus, the established strategies for the preparation of axially functionalized titanium phthalocyanines with the unsubstituted macrocyclic ligand Pc could not be properly transferred to the chemistry of soluble Pc# complexes.

Since, for example, imido functionalized Pc# compounds were not accessible in pure form starting from **1**, we developed a different synthetic protocol starting from the dichlorido species [Pc#TiCl$_2$] **5**.

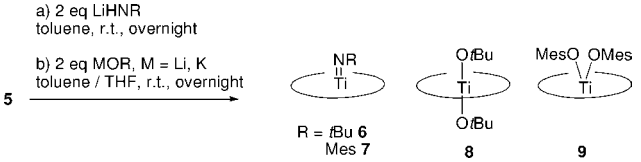
5 could be obtained by reductive cyclotetramerization of 6,7-dicyano-1,1,4,4-tetramethyltetraline in the presence of $TiCl_4$ in chloronaphthalene (Scheme 2). **5** is a versatile precursor for the preparation of axially functionalized, soluble phthalocyanines. The reaction with 2 equiv of primary lithium amides leads to the respective alkyl or aryl imido complexes [Pc#Ti(N*t*Bu)] **6**

Scheme 2. Preparation of 5



and [Pc#Ti(NMes)] **7** under mild conditions. Similarly, salt elimination reactions with lithium or potassium alkoxides produces the bisalkoxo complexes *trans*-[Pc#Ti(O*t*Bu)$_2$] **8** and *cis*-[Pc#Ti(OMes)$_2$] **9** (Scheme 3). The cis and trans isomers

Scheme 3. Preparation of Axially Functionalized Titanium Phthalocyanines 6−9 via Salt Elimination[a]



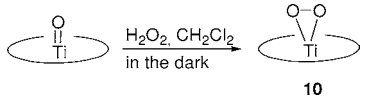
[a]The ellipse represents the macrocyclic ligand.

can be distinguished by ^{1}H NMR spectroscopy (see Spectroscopy section). According to NMR spectroscopy **8** decomposes rapidly in solution to form oxido complex **1**, which is attributed to the elimination of isobutene forming unstable [Pc#Ti(OH)-(O*t*Bu)] or [Pc#Ti(OH)$_2$], which readily eliminate *t*BuOH or water. Both alkoxo compounds are extremely labile toward hydrolysis. Attempts to synthesize bisalkyl or bisamido complexes by the reaction of [Pc#TiCl$_2$] with lithium alkyls or secondary lithium amides were unsuccessful because of the side reaction of *ortho*-directed deprotonation of the phthalocyanine backbone.[50,51]

Oxido, Sulfido, and Selenido Derivatives. To study the higher homologues of the parent titanium oxo and peroxo Pc#, we were particularly interested in the synthesis of mono- and dichalcogenido compounds [Pc#TiE] (E = O (**1**), S (**12**), Se (**14**)) and [Pc#Ti(E$_2$)] (E = O (**10**), S (**11**), Se (**13**)).

Peroxido compound [Pc#Ti(O$_2$)] **10** could be successfully synthesized by treatment of a dichloromethane solution of [Pc#TiO] with H_2O_2 in the dark (Scheme 4). The identity of

Scheme 4. Preparation of [Pc#Ti(O$_2$)] 10



the product was confirmed by UV−vis, NMR, and IR spectroscopy. The characteristic $\upsilon_{Ti=O}$ = 977 cm^{-1} disappears, and three absorptions for the peroxo group are observed (υ_{O-O} = 895 cm^{-1}, $\upsilon_{Ti-O\ sym}$ = 642 cm^{-1}, and $\upsilon_{Ti-O\ asym}$ = 609 cm^{-1}). The product readily decomposes when exposed to light, leading to decomposition of the macrocyclic ligand. This is also the case for related titanium peroxo porphyrins.[16]

In the case of the porphyrin analogues, subvalent Ti(II) species could be oxidized by elemental sulfur or selenium,

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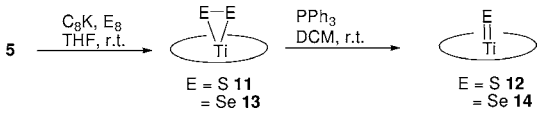
yielding the dichalcogenido compounds. Analogously, oxidation by R_3PE gave the monochalcogenido compounds.[12] $[Pc^{\#}TiCl_2]$ could not be reduced to a subvalent Ti(II) species by reaction with LAH or $LiHBEt_3$ like the corresponding porphyrins.[12,15] These reactions were unselective. We attribute this to the nucleophilic character of these reducing agents which can attack the imine bridge between the isoindoline units. Thus, we had to develop a different synthetic approach. The dichalcogenido compounds **11** and **13** could be obtained by an in situ protocol employing **5**, C_8K and S_8 and Se_8, respectively (Scheme 5). It

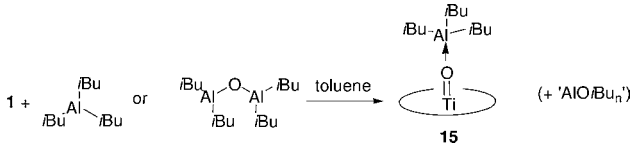
Scheme 5. Preparation of Dichalcogenido and Chalcogenido Compounds 11−14



cannot be ruled out that under these conditions the reduction of E_8 to K_2E_x is a parallel reaction to the reduction of the metal phthalocyanine, but both possible pathways lead to the same products. A selective synthesis of the monochalcogenido species **12** and **14** was possible by reduction of the dichalcogenido compounds **11** and **13** with an excess of Ph_3P. The reaction progress could be followed by ^{31}P NMR or UV−vis spectroscopy, and complete conversion was achieved after 5 min.

Lewis Acid Adducts. A different class of axially substituted titanium phthalocyanines are Lewis acid adducts of $[Pc^{\#}TiO]$. Similar experiments have been described by the group of Hanack for rhenium nitrido Pcs and various group 3 Lewis acids.[52] In our case, a Lewis acid adduct can be readily obtained by adding tri*iso*butylaluminium or tetra*iso*butyldialumoxane to toluene solutions of **1** (Scheme 6). The instantaneous

Scheme 6. Preparation of Lewis Acid Adduct 15



formation of the product can be monitored via NMR and UV−vis spectroscopy. In both cases, the same product of the constitution $[Pc^{\#}TiO{\rightarrow}Al(i\mathrm{Bu})_3]$ (**15**) is obtained. This is due to ligand redistribution in the case of $(i\mathrm{Bu})_2AlOAl(i\mathrm{Bu})_2$ leading to the in situ formation of $Al(i\mathrm{Bu})_3$ and formally "$AlO(i\mathrm{Bu})_n$". A new set of $Pc^{\#}$ resonances is observed in the ^1H NMR spectrum together with the upfield shifted resonances of the axially coordinated Lewis acid. Also, the Q-band maximum in the electronic spectra is shifted, and the characteristic $\nu_{Ti=O}$ at 977 cm^{-1} is shifted to lower wavenumbers, which is in accordance with a reduction of the Ti−O bond strength.

Spectroscopy. *NMR Spectra.* All proton NMR spectra show the characteristic downfield shift for the phthalocyanine protons (9.29−10.06 ppm).[31,53] Since no other signals occur in this region, the singlet observed for the eight $Pc^{\#}$ ring protons is a suitable NMR probe for the selectivity of a reaction. The free ligand and its dialkali salts **2**−**4** show a single resonance for the methyl groups, indicating the D_{2h} and D_{4h} symmetry of the substances, respectively. The C_{4v} symmetric titanium complexes (**1**, **5**−**7**, **9**−**15**) show two signals for the methyl group, which results from the symmetry lowering imposed by the axial ligands.[40] For dichlorido compound **5** and bisaryloxido compounds **9**, this suggests a cis arrangement of the functional groups. In the case bisalkoxido compound **8** a single resonance for the methyl groups is observed, indicating a D_{4h} symmetric trans arrangement of the bulky O*t*Bu-groups. This is in accordance with $[PcTi(OSiPh_3)_2]$,[37] were the bulky substituents are also arranged in a trans fashion. All resonances of axial ligands are shifted upfield because of the strong ring current in the macrocyclic ligand.[31]

UV−vis Spectra. UV−vis spectra of all substances were measured in dry CH_2Cl_2 or toluene. The electronic spectrum of the free ligand $[Pc^{\#}H_2]$ shows a split Q-band with maxima at 710 and 676 nm which is characteristic for D_{2h} symmetric phthalocyanines.[54] The deprotonated species **2**−**4** show a single Q-band at 680−683 nm which is in accordance with the assumed D_{4h} symmetry of the molecules. The electronic spectra of the axially functionalized titanium phthalocyanines **1**, **5**−**11**, and **13** all show the characteristic Q-band absorption maximum between 710 and 717 nm. No significant changes are observed upon exchange of the axial functionality. This is because the absorption spectra are mainly determined by the macrocyclic ligand system.[23,31,32,39] Representative for all prepared compounds, the spectra of $[Pc^{\#}H_2]$, $[Pc^{\#}K_2]$ and $[Pc^{\#}TiCl_2]$ are displayed in Figure 2.

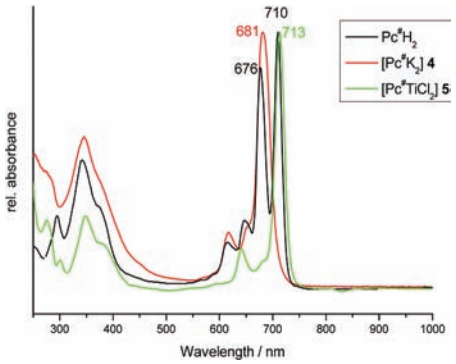


Figure 2. UV−vis spectra of $Pc^{\#}H_2$, $[Pc^{\#}K_2]$, and $[Pc^{\#}TiCl_2]$ in CH_2Cl_2.

We were particularly interested in the effect that the heavier axial ligands S^{2-} and Se^{2-} have on the photophysical properties of the complexes. The reactions of **11** and **13** with PPh_3 were therefore monitored via UV−vis spectroscopy. In fact, pronounced changes in the electronic spectra are observed as the Q-band maxima are shifted bathochromically from 717 nm (**11**) to 726 nm (**12**) and from 716 (**13**) to 736 nm (**14**), respectively. The reactions are complete after a few minutes (for spectra see Supporting Information). This may be attributed to the higher polarizability of the large, soft axial ligand.

Upon addition of $Al(i\mathrm{Bu}_3)$ to a toluene solution of **1** the formation of Lewis acid adduct **15** can be detected by UV−vis spectroscopy within 30 s. The Q-band maximum is shifted to 731 nm and decreases in intensity. A similar behavior was described for Lewis acid adducts of $[R_8PcReN]$.[52] Addition of traces of protic solvent (MeOH) results in the immediate dissociation of the adduct, and the stating material is recovered (for spectra see Supporting Information).

Reactivity. The group of Woo investigated the reactivity of titanium imido porphyrins toward different subtrates.[11]

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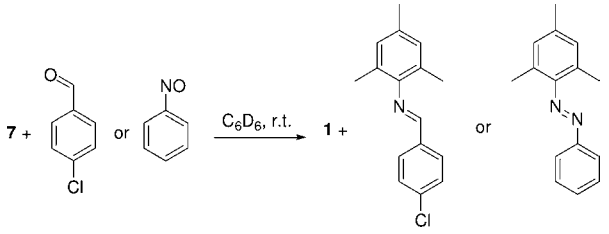
Compare these results with the reactivity of the corresponding phthalocyanines we carried out nitrene transfer reactions using **7**, *p*-chlorobenzaldehyde, nitrosobenze, triphenylphosphine oxide, and styrene oxide as substrates (Scheme 7). The

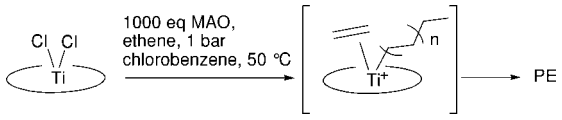
Scheme 7. Nitrene Transfer Reaction of 7



progress of the reactions was monitored via NMR spectroscopy, and the identity of the products was confirmed by electrospray ionization (ESI) HRMS spectrometry. No reaction was observed with triphenylphosphine oxide and styrene oxide. In the case of *p*-chlorobenzaldehyde, the imido group transfer was incomplete after 24 h at room temperature. According to ^{1}H NMR spectroscopy, a mixture of 70% [Pc$^{\#}$Ti(NMes)] and 30% [Pc$^{\#}$TiO] was present and no further reaction occurred. Still, the formation of *p*-chlorobenzylidene mesitylamine was unambiguously confirmed by ESI HRMS. This compares well with the result for corresponding porphyrins where complete nitrene transfer to *p*-chlorobenzaldehyde only occurred after 4 weeks or in the presence of excess substrate.[11] Upon addition of nitrosobenzene to a solution of **7** in C_6D_6, complete consumption of the starting materials and synchronous formation of mesityl phenyl diazene occurred within 5 min. These results show that the reactivity of titanium imido phthalocyanines toward nitrene transfer is comparable to corresponding titanium imido porphyrins.

Some examples of phthalocyanines used in polymerization catalysis have been described in the literature.[55−58] For example, it has been reported that soluble vanadyl and nickel naphthalocyanines can polymerize ethene at high pressure.[59] Because of the cis arrangement of the chlorido ligands, **5** seemed a suitable precatalyst for olefin polymerization (Scheme 8). We therefore tested the activity of dichlorido compound **5**

Scheme 8. Poymerization of Ethene Using 5



and titanyl Pc **1** in the polymerization of ethene at atmospheric pressure using 1000 equiv of MAO as cocatalyst. For comparison we also employed Eurecen 5031 [Zr^{IV}(*n*BuC$_5$H$_4$)$_2$Cl$_2$] as precatalyst under the same conditions. The results of the polymerization experiments are summarized in Table 1. Taking into account that the experiments were conducted at atmospheric pressure, these results show that the catalytic activity of the dichlorido compound is significantly higher than for the titanyl and vanadyl species.[59] Yet, the activities are much lower than for well established ethene polymerization catalysts such as Eurecen 5031. Still, these results show that the reactivity of the central titanium atom in soluble phthalocyanine complexes is in principle comparable to that in other titanium complexes.

Table 1. Polymerization of Ethene[a]

precatalyst	*t*/h	*p*/bar	$m_{polymer}$/g	T_m/°C	activity/ g mol^{-1} h^{-1} bar^{-1}
[Pc$^{\#}$TiCl$_2$][b]	1	1	0.27	137	27
[Pc$^{\#}$TiO][b]	1	1	0.01	134	1
[NPcVO][c]	4	48	1.00		0.5
Eurecen 5031[b]	0.5	1	1.782	133	356

[a]Reaction conditions. [b]n_{cat} = 10 μmol, n_{MAO} = 10 mmol, 1000 equiv, in 50 mL of chlorobenzene, 50 °C. [c]Ref 59; n_{cat} = 10 μmol, n_{MAO} = 1 mmol, 100 equiv, in 10 mL of chlorobenzene in a 120 mL glass lined autoclave, 50 °C.

Crystal Structures of Pc$^{\#}$H$_2$, 1 and 5. In addition to the crystal structure of [Pc$^{\#}$TiO] **1**·3CHCl$_3$ reported previously,[40] we were able to obtain slightly different structures by crystallization from dichloromethane and benzene (see Supporting Information). In all cases, a coplanar arrangement of the macrocycles is present independently of the incorporated solvent. We do not observe face-to-face dimers which are typically found in highly aggregating derivatives of unsubstituted chromophore complexes [PcTiO].[2,39,60] No significant changes of bond lengths and angles within the molecules are found. The different solvent molecules incorporated in the lattice cause minor differences in the packing and the intermolecular distances.

The free ligand Pc$^{\#}$H$_2$ was crystallized by layering a toluene solution with pentane in the absence of air, moisture, and light.[61] Pc$^{\#}$H$_2$ crystallizes in the trigonal space group $R\bar{3}$ with three molecules per unit cell. The molecular structure is displayed in Figure 3. Toluene and disordered molecules of

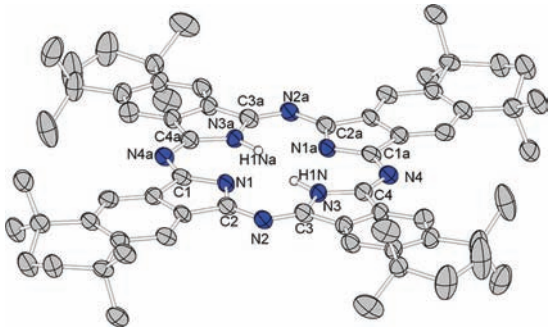


Figure 3. Molecular structure of Pc$^{\#}$H$_2$. Ellipsoids are shown at 30% probability. H atoms (except N*H*) are omitted for clarity. Symmetry operation used to generate equivalent atoms: a = −*x*+1/3,−*y*+2/3,−*z*+2/3.

pentane are included in the molecular packing. The molecule possesses an inversion center. The aromatic heterocycle is essentially planar, and the annulated cyclohexene rings adopt a twist-boat conformation. Because of intramolecular hydrogen bonds, the NH protons do not lie on the N3−N3a axis but are oriented toward N1. The bond lengths and angles of the Pc core compare well to the values reported for unsubstituted PcH$_2$.[62−64] Selected bond lengths and angles are summarized in Table 2. Crystallographic data are summarized in Table 3.

The molecular packing of Pc$^{\#}$H$_2$ is shown in Figure 4. The three molecules present in the unit cell are oriented almost perpendicular with respect to each other (angle between N$_4$ planes = 88.3(1)°). This kind of arrangement has not been described for any of the polymorphs of PcH$_2$, where either two or four orientations of the macrocycles are present.[62−64]

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for $Pc^{\#}H_2$

C1−N1	1.369(6)	N3−H1N	0.95(5)
N1−C2	1.383(6)	C4−N4	1.326(6)
C2−N2	1.339(6)	N4−C1a	1.347(6)
N2−C3	1.320(6)	C3−N3−H1N	112(4)
C3−N3	1.392(7)	C4−N3−H1N	136(4)
N3−C4	1.353(6)		

Table 3. Crystal Data and Structure Refinement for $Pc^{\#}H_2$ and 5

	$Pc^{\#}H_2$	5
formula	$C_{239}H_{282}N_{24}$	$C_{135}H_{158}Cl_{18}N_{16}Ti_2$
fw	3490.89	2738.62
crystal system	trigonal	cubic
space group	$R\bar{3}$	$Im\bar{3}$
a, Å	32.4964(18)	28.953(4)
b, Å	32.4964(18)	28.953(4)
c, Å	16.3282(10)	28.953(4)
α, deg	90	90
β, deg	90	90
γ, deg	120	90
V, Å^3	14932.7(15)	24270(6)
Z	3	6
D_{calcd}, g/cm^3	1.165	1.124
μ, cm^{-1}	0.068	0.442
$F(000)$	5652	8580
crystal size, mm^3	0.21× 0.21× 0.03	0.24× 0.21× 0.03
reflns collected	18941	4563
independent reflns	7016	4563
R_{int}	0.0960	0.0000
R indices $[I > 2\sigma(I)]^a$	R_1 = 0.0586	R_1 = 0.0613
	wR_2 = 0.1043	wR_2 = 0.1399
R indices (all data)	R_1 = 0.3209	R_1 = 0.1472
	wR_2 = 0.1782	wR_2 = 0.1601

$^a R_1 = [\sum||F_o| - |F_c||/\sum|F_o|]$; $wR_2 = \{[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^4)]^{1/2}\}$.

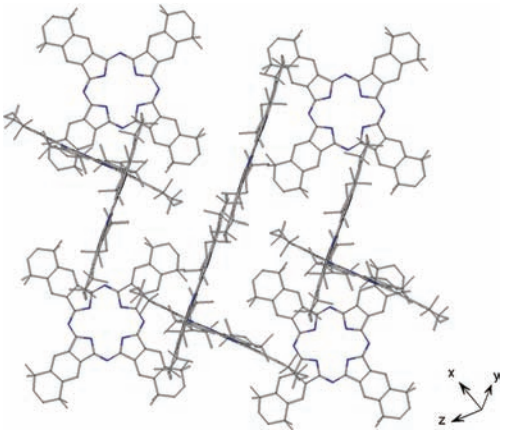

Figure 4. Molecular packing of $Pc^{\#}H_2$. Solvent molecules and H atoms are omitted for clarity.

5 crystallizes from a saturated dichloromethane solution in the cubic space group $Im\bar{3}$. The crystal structure of **5** is displayed in Figure 5. Crystallographic data are summarized in Table 3. Because of the symmetry of the molecule, only one isoindoline moiety is present in the asymmetric unit. Also, the twist-boat conformation of the annellated cyclohexene rings is

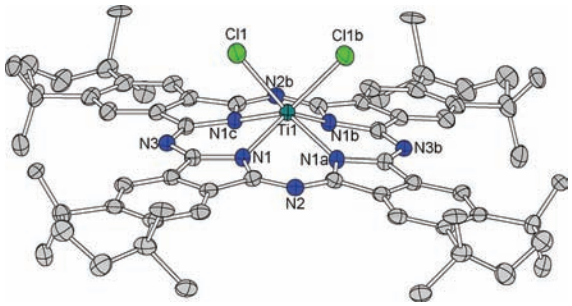

Figure 5. Molecular structure of **5**. Ellipsoids are shown at 30% probability. Disorder of the cyclohexene rings and H atoms are omitted for clarity. Symmetry operations used to generate equivalent atoms: a: x, $-y+1$, z; b: $-x$, $-y+1$, z; c: $-x$, y, z.

disordered. The two chlorido atoms are located on the same side of the macrocycle in a cis arrangement, which is also present in $[PcTiCl_2]$. The chlorido ligands lie on the N3−Ti−N3b plane. The Ti1−Cl1 bond length is 2.328(2) Å and is slightly longer than in $[PcTiCl_2]$ (2.309(6) and 2.324(5) Å). The titanium atom is displaced from the N1-plane toward the chlorido ligands about 0.834 Å. Thus, the displacement is comparable to the structure of $[PcTiCl_2]$ (0.84 Å)[30] and larger than in $[Pc^{\#}TiO]$ (0.748 Å).[40] The coordination around the titanium atom is trigonal prismatic. Selected bond lengths and angles are summarized in Table 4. The values compare well

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 5 and $[PcTiCl_2]$

	5	$[PcTiCl_2]^a$
Ti1−Cl1	2.328(2)	2.324(5), 2.309(6)
Ti1−N1	2.086(3)	2.090(13), 2.095(9), 2.060(10), 2.106(10)
Cl1−Ti1−Cl1a	81.7(1)	82.41(19)
N1−Ti1−Cl1	83.5(1)	88.0(3), 79.4(3), 80.8(4), 87.4(4)
N1a−Ti1-Cl1	135.9(1)	127.0(4), 127.8(3), 145.1(3), 143.7(4)
N1−Ti1−N1a	78.8(2)	78.7(4), 79.1(4)
N1−Ti1−N1b	132.9 (2)	135.7(5), 129.6(5)

^{a}The values refer to the corresponding bond lengths and angles.

with those found for the unsubstituted phthalocyanine complex $[PcTiCl_2]$. The macrocyle deviates slightly from planarity, adapting a "saucer" type structure.[2]

Figure 6 shows the molecular arrangement within the unit cell. The macrocycles are arranged as face-to-face dimers, and neighboring dimers are aligned essentially perpendicular to each other. In contrast to this, in the structures of the related compounds $[PcTiCl_2]$[30] and $[Pc^{\#}TiO]$[40] layered arrangements are present, where all the macrocycles lie essentially parallel. It has been found that only the polymorphs exhibiting the colinear arrangement can be applied in semiconducting devices.[65] Therefore, **5** is not expected to show good semiconducting properties in the presented crystal phase. Solid state fluorescence spectroscopy could show whether the dimeric arrangement leads to fluorescence quenching, and comparison of the fluorescence properties of $[Pc^{\#}TiCl_2]$ and $[Pc^{\#}TiO]$ in solid state are therefore of interest.

CONCLUSIONS

In this work we describe the synthesis of various soluble, axially substituted titanium phthalocyanines under mild conditions. Oxido compound **1** could be converted into peroxido species

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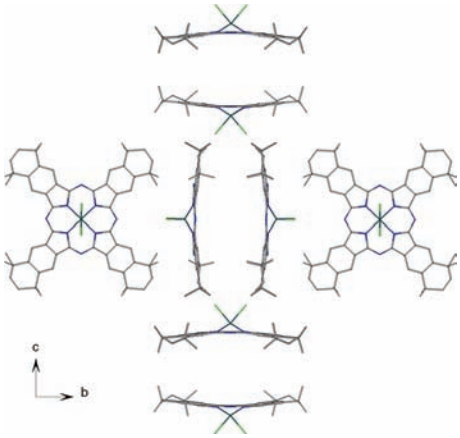

Figure 6. Molecular packing of [Pc#TiCl$_2$] **5**. Disorder of the cyclohexene rings, 3.5 disordered molecules of dichloromethane per **5**, and H atoms are omitted for clarity.

10 and Lewis acid adduct **15**. [Pc#TiCl$_2$] **5** is a versatile precursor for the introduction of various functionalities, such as imido (**6**, 7), alkoxido and aryloxido (**8**, **9**), sulfido **12**, disulfido **11**, selenido **14**, and diselenido **13**. In most cases the photophysical properties of the prepared compounds are very similar, and the nature of the axial ligand has no significant effect on the Q-band maximum. In contrast to this, the Q-band maxima are shifted bathochromically in the cases of the higher homologues of [Pc#TiO] **1**, [Pc#TiS] **12**, and [Pc#TiSe] **14**, respectively. The reactivity of selected functionalized Pcs in atom group transfer reactions and ethene polymerization has been demonstrated. The crystal structures of the free ligand Pc#H$_2$, **1**, and **5** reveal different arrangements of the macrocyclic systems (coplanar, three-dimensional, and dimeric), which should affect the photophysical properties of the dyes in solid state. Our next goal is to investigate how the different axial functionalities may be employed to anchor these nonaggregating phthalocyanine chromophores to different wide band gap metal oxide semiconductor surfaces and thus prepare optoelectronic devices.

■ ASSOCIATED CONTENT

Supporting Information

(1) UV−vis spectra, (2) NMR spectra, (3) crystal structures of **1**, (4) crystallographic information files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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