Imidotitanium Complexes with Heteroallylic Ligands: Synthesis and Solid-State Structure

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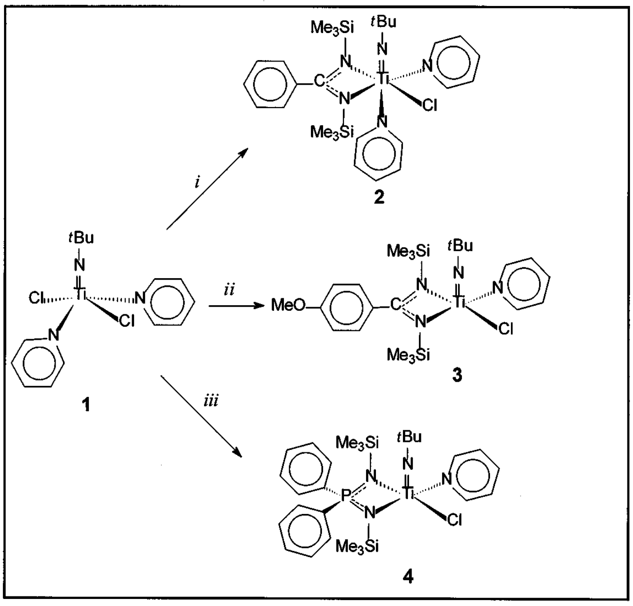
Treatment of $Ti(NtBu)Cl_2(py)_2$ (**1**, py = pyridine) with bulky heteroallylic ligands in a 1:1 molar ratio affords the monosubstituted derivatives $[PhC(NSiMe_3)_2]Ti(NtBu)Cl(py)_2$ (**2**), $[MeOC_6H_4C(NSiMe_3)_2]Ti(NtBu)Cl(py)$ (**3**), and $[Ph_2P(NSiMe_3)_2]Ti(NtBu)Cl(py)$ (**4**). Similarly, 2:1 reactions afforded the disubstitution products $[PhC(NiPr)_2]_2Ti(NtBu)(py)$ (**6**) and $[Ph_2P(NSiMe_3)_2]_2Ti(NtBu)$ (**7**). The bis(pyridine) adduct $Ph_2P(NSiMe_3)_2Li(py)_2$ (**5**) was isolated as a by-product during the preparation of **4**. The molecular structures of **7** has been established by X-ray crystallography.

The chemistry of transition metal imido complexes continues to be an area of active research.[1−3] Such compounds are of interest as intermediates in organic syntheses as well as catalytically active species.[4−19] Just a few years ago, imidotitanium(IV) complexes were exceedingly rare. The first well characterized monomeric imidotitanium species were reported independently at the same time by Roesky et al. and Rothwell et al. in 1990.[20,21] Following the initial work, various other monomeric and dimeric imido derivatives of titanium have been prepared.[22−30] However, a general route providing straightforward access to a series of Ti=NR species was lacking. The recent preparation of readily accessible precursors such as $Ti(NtBu)Cl_2(py)_2$ (**1**, py = pyridine) and $Ti(NtBu)Cl_2(tBu\text{-}py)_2$ (*t*Bu-py = 4-*tert*-butylpyridine) has greatly facilitated the investigation of these compounds.[31] Various complexes derived from these starting materials have recently been reported by Mountford et al.[31−35] We describe here the synthesis and structural characterization of imidotitanium(IV) complexes containing bulky heteroallylic ligands. Related complexes have so far been reported only for vanadium(V) and niobium(V).[36] The bulky heteroallylic ligands used in this study include the benzamidinate anions $[PhC(NSiMe_3)_2]^-$, $[MeOC_6H_4C(NSiMe_3)_2]^-$, and $[PhC(NiPr)_2]^-$ as well as the diiminophosphinate anion $[Ph_2P(NSiMe_3)_2]^-$.[37−40] Chelating ligands of this type are currently being investigated as alternatives for cyclopentadienyl ligands in the design of novel "metallocene-like" homogeneous catalysts.[41−50]

Syntheses and Structures

Compound **1** is easily made be reacting $TiCl_4$ with *tert*-butylamine in the presence of pyridine.[31−35] Subsequent treatment of **1** with lithium salts of bulky heteroallylic anions in THF solution in a 1:1 molar ratio resulted in formation of the monosubstitution products **2**−**4** (Scheme 1).

Scheme 1. Reaction conditions: *i)* $Li[PhC(NSiMe_3)_2]$, 1 equiv., THF, 20°C; *ii)* $Li[MeOC_6H_4C{-}(NSiMe_3)_2]$, 1 equiv., THF, 20°C; *iii)* $Li[Ph_2P(NSiMe_3)_2]$, 1 equiv., THF, 20°C

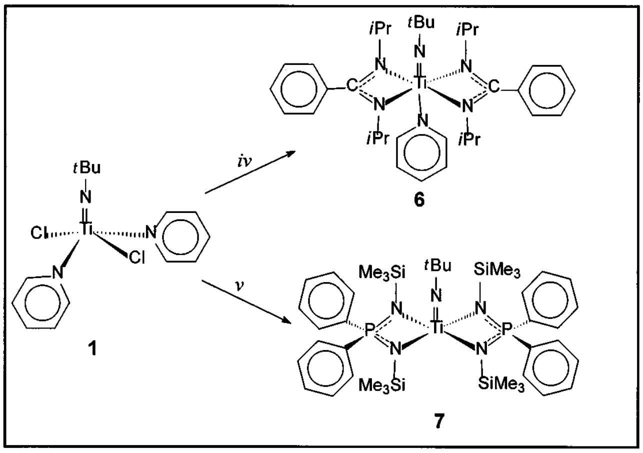


The monosubstituted complexes **2**−**4** form orange crystalline solids, which are soluble in THF or toluene and only marginally soluble in hexane or acetonitrile. All three compounds were fully characterized by elemental analyses and spectroscopic methods. The benzamidinate derivative **2** is obtained as a bis(pyridine) adduct, while the complexes **3** and **4** contain only one additional pyridine ligand. In addition to the NMR spectroscopic results, the pyridine content of each compound was independently established by GC analysis of hydrolyzed samples. In the case of **2** X-ray quality crystals were grown from a saturated hexane solution. Unfortunately, due to the low quality of all examined crystals, the structure determination was not sufficiently accurate to allow a detailed discussion of bond lengths and angles. However, the crystallographic results confirm the overall structure of **2** as a monomeric *tert*-butylimidotitanium(IV) complex containing one silylated benzamidinate ligand and one chloro function (cf. Scheme 1).

The preparation of **4** from **1** and Li[$Ph_2P(NSiMe_3)_2$][47–51] in THF solution is generally accompanied by the formation of the by-product $Ph_2P(NSiMe_3)_2Li(THF)_2$ (**5**), which can be isolated by fractional crystallization from hexane, in which it is less soluble than the titanium complex **4**.[51a] Compound **5** forms pale yellow, moisture sensitive crystals. Its molecular structure can be formulated in analogy to the crystallographically characterized THF adduct $Ph_2P(NSiMe_3)_2Li(THF)_2$.[51b] The presence of two pyridine ligands in **5** was further confirmed by a gas chromatographic analysis following hydrolysis of the material.

Similar treatment of **1** with two equivalents of heteroallylic ligands results in clean formation of the disubstituted derivatives **6** and **7** (Scheme 2).

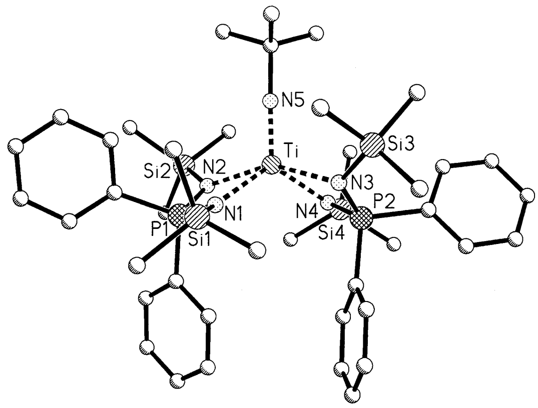
Scheme 2. Reaction conditions: *iv)* Li[PhC(N*i*Pr)$_2$], 2 equiv., THF, 20°C; *v)* Li[$Ph_2P(NSiMe_3)_2$], 2 equiv., THF, 20°C



Once again the composition of the products depends on subtle differences in the steric bulk of the heteroallylic ligands. The benzamidinate derivative **6** is obtained as the mono-pyridine solvate, while **7** is an unsolvated, pentacoordinated imidotitanium(IV) species. The complexes are isolated as nicely crystalline, orange or red materials, which are readily susceptible to hydrolysis in the presence of moist air. They exhibit a high solubility in non-polar organic solvents such as toluene or hexane. Both complexes were fully characterized by elemental analyses and spectroscopic methods.

The molecular structure of **7** (Figure 1) was determined by X-ray diffraction. Red single crystals of the compound were grown by slow cooling of a saturated solution in hexane to −20°C. The crystallographic investigation confirms the presence of a monomeric, pentacoordinated imidotitanium complex, in which the central titanium atom is coordinated only to nitrogen. A comparable coordination environment was found for *tert*-butylimidotitanium species containing the aza-macrocyclic ligands tetra- and octamethyldibenzotetraaza[14]annulene (Me4taa and Me8taa, respectively).[31] With 1.680(4) Å the Ti=N bond length falls in the typical range found for other crystallographically characterized imidotitanium complexes (1.672(7)−1.723(4) Å).[35] The Ti−N−C(*t*Bu) angle [175.9(3)°] is much closer to linearity than that in the macrocyclic imidotitanium derivative (Me8taa)Ti(N*t*Bu) [164.3(3)°].[31] The *tert*-butylimido ligand can thus be assumed to act as four-electron donor towards titanium.

Figure 1. Molecular structure of [$Ph_2P(NSiMe_3)_2$]Ti(N*t*Bu) (**7**)[a]



[a] Selected bond lengths [Å] and angles [°]: Ti−N(1) 2.152(5), Ti−N(2) 2.201(4), Ti−N(3) 2.203(5), Ti−N(4) 2.146(5), Ti−N(5) 1.680(4), P(1)−N(1) 1.605(4), P(1)−N(2) 1.596(4), P(2)−N(3) 1.597(4), P(2)−N(4) 1.607(4), N(5)−C(37) 1.481(6), Ti−N(5)−C(37) 175.9(3), N(1)−P(1)−N(2) 103.9(2), N(3)−P(2)−N(4) 104.0(2).

IR Studies

The compounds **2**−**4** and **6**, **7** have also been closely examined by IR and Raman spectroscopy. Assignment of the IR bands was made by spectra comparison as well as by inclusion of the Raman spectra and literature data. The N−C−N chelating units in **2**, **3**, and **6** give rise to a ν_{as} CN_2 band at 1523−1516 cm^{-1} as well as the ν_s CN_2 at 1377−1372 cm^{-1}.[52] The ν_{as} PN_2 vibration in **4** and **7** is assigned to the bands at 1090 and 1095 cm^{-1}, respectively.[53] The $SiMe_3$ groups in **2**−**4** and **7** are characterized by the following bands: δ_{as} CH_3 at 1407−1400 cm^{-1}, δ_s CH_3 at 1249−1245 cm^{-1}, and CH_3 rocking at 770−751 cm^{-1}.[54] Characteristic for the phenyl rings in all compounds are the ring valence vibrations at 1609−1600 cm^{-1} (only **7** shows no absorption in this region), 1592−1572 cm^{-1} and 1485−1477 cm^{-1} as well as the rocking vibrations at 1072−1062 cm^{-1} and at 1034−1028 cm^{-1}. A doublet at 1377−1372 and 1390−1385 cm^{-1} was assigned to δ_s CH_3 of the *tert*-butyl group in the *tert*-butylimido ligand. In addition, the Raman spectra show at 653−651 cm^{-1} the ν_s (N)−CC_3 vibration of the N−$C(CH_3)_3$ unit.[55] ν Ti−py bands are observed in the spectra of **2−4** and **6** at 282−280 cm^{-1}.[56] In addition, the Raman spectra exhibit a ν CH band at 3082−3074 cm^{-1}, which can be assigned to pyridine. In the case of the monosubstituted complexes **2−4** the ν TiCl vibrations are observed at 323−321 cm^{-1} (IR) and 328−329 cm^{-1} (Raman), respectively. The isopropyl substituents in **6** give rise to the ν CH band at 1386 cm^{-1} in the IR spectrum as well as bands at 2926 cm^{-1} (ν CH), 2869 cm^{-1} (ν_s CH_3) and 480 cm^{-1} (δ CC_2) in the Raman spectrum.[55] Bands at 2838 cm^{-1} (ν_s CH_3), 1293 and 1040 cm^{-1} (ν CO) in the IR spectrum of **3** are typical for the *p*-methoxy substituent.[53]

Conclusions

In summary, we have shown that monomeric imidotitanium complexes containing bulky heteroallylic ligands can be synthesized starting from the readily accessible precursor $Ti(NtBu)Cl_2(py)_2$ (**1**). Depending on the stoichiometry of the starting materials, 1:1- and 1:2 derivatives can be isolated. Bulky benzamidinate ligands as well as diiminophosphinate anions are equally suited to stabilize monomeric imidotitanium complexes.

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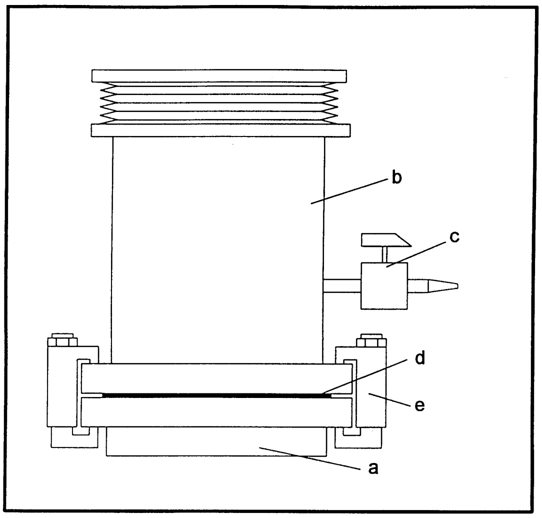
Experimental Section

All reactions were carried out under purified nitrogen using standard Schlenk-line or dry-box techniques. Solvents were carefully dried over Na/benzophenone and freshly distilled under nitrogen prior to use. − Infrared and Raman spectra were recorded using a Perkin Elmer FTIR-2000 spectrometer equipped with a Raman facility. The IR measurements in the spectral range of 400−200 cm^{-1} were carried out using either Nujol mulls or with the pellet technique using RbBr as embedding medium. KBr pellets were used for spectra in the 4000−400 cm^{-1} range. For this purpose a metal bellow vessel was designed, which greatly facilitates the IR investigation of air-sensitive samples, especially in connection with the dry box technique. A diagram of the vessel is depicted in Figure 2.

Figure 2. Diagram of the metal bellow vessel. a) base plate, b) cap with metal bellow, c) isolating valve, d) packing ring, e) clamp



The KBr die containing the air- and moisture-sensitive samples was placed under inert atmosphere in the dry-box into the evacuable metal bellow vessel made of steel. The metal bellow serves to level out the height difference of the vessel during power transmission from the hydraulic press onto the KBr die. The vessel is taken out of the dry box and evacuated to ca 10^{-2} mbar. After pressing the pellet the evacuated vessel is taken back into the dry box. The pellet holder containing the pellet is closed air-tight on both sides using IR cell windows and sealing rings, and then taken out of the dry box and inserted into the spectrometer. Very weak bands are not listed in the IR data. − NMR spectra: Bruker AM 250. − X-ray crystallography: Intensities were collected at −100°C on a Nonius CAD4 diffractometer with graphite-monochromated Cu-K_α radiation (λ = 1.54178 Å). The structure was solved by direct methods with SHELXS-86 and refined by full-matrix least-squares procedures using SHELXL-93.[57] A riding model was employed to refine the hydrogen atom positions. − The starting materials $Ti(NtBu)Cl_2(py)_2$ (**1**),[31][35] $Li[RC_6H_4C(NSiMe_3)_2]$ (R = H, MeO),[58] $Li[PhC(NiPr)_2]$[46] and $Li[Ph_2P(NSiMe_3)_2]$[47,48] were prepared according to literature procedures.

Reactions of $Ti(NtBu)Cl_2(py)_2$ (1) with Heteroallylic Ligands (General Procedure): To a stirred solution of 1.74 g (5.0 mmol) of **1** in 20 ml of THF is added dropwise at room temperature a solution of 5.0 mmol of the ligand in 30 ml of THF (1:1 reactions). For the 1:2 reactions a solution of 10.0 mmol of the ligand in 60 ml of THF is employed. Stirring at room temperature is continued for 8 h and the mixture is evaporated to dryness. The residue is extracted with 40 ml of boiling hexane and filtered while hot through a thin layer of Celite filter aid. Cooling to −20°C for 24 h affords the crude product, which is purified by recrystallization from hexane.

[N,N'-Bis(trimethylsilyl)benzamidinato]-N-tert-butylimidochlorobis(pyridine)titanium(IV) (**2**): Red crystals, m.p. 107−109°C. Yield: 1.36 g (48%). − IR (cm^{-1}): $\tilde{\nu}$ = 2595 s, 2915 m, 2897 m, 1604 m, 1592 w, 1520 m, 1510 w, 1479 m, 1459 m, 1444 m, 1426 m, 1406 m, 1385 (sh) w, 1376 m, 1358 m, 1247 vs, 1027 w, 1042 m, 1029 w, 1013 m, 1002 m, 985 s, 921 s, 840 vs, 785 m, 759 s, 728 m, 700 s, 632 m, 526 m, 508 m, 492 m, 456 w, 392 w, 353 w, 302 w, 280 w. − ^{1}H NMR (C_6D_6): δ = 9.54 (m, 2 H, *p*-C_5H_5N), 8.70 (m, 4 H, *m*-C_5H_5N), 7.01 (m, 4 H, *o*-C_5H_5N), 6.90 (m, 1 H, *p*-C_6H_5), 6.65 (m, 4 H, *o,m*-C_6H_5), 1.35 (s br, 9 H, *t*Bu), 0.35 (s br, 18 H, $SiMe_3$). EI MS (70 eV); *m/z* (%): 567 (1) [M$^+$], 510 (2) [$M^+ - C_4H_9$], 263 (49) [$PhC(NSiMe_3)_2^+$], 103 (44) [$PhCN^+$], 73 (100) [$SiMe_3^+$]. − $C_{27}H_{42}ClN_5Si_2Ti$ (567.17): calcd. C 56.29, H 7.35, N 12.16; found C 55.83, H 7.82, N 11.88.

[N,N'-Bis(trimethylsilyl)-p-methoxybenzamidinato]-N-tert-butylimidochloro(pyridine)titanium(IV) (**3**): Red-brown crystals, m.p. 88−90°C. Yield: 1.34 g (51%). − IR (cm^{-1}): $\tilde{\nu}$ = 3069 w, 2954 m, 2897 m, 2838 w, 1609 s, 1583 w, 1516 m, 1489 m, 1477 m, 1459 m, 1443 s, 1425 (sh) s, 1400 m, 1390 (sh) m, 1377 m, 1350 m, 1300 (sh) w, 1293 m, 1249 s, 1171 m, 1108 m, 1071 w, 1040 (sh) m, 1034 m, 1016 s, 993 (sh) s, 983 s, 914 m, 839 vs, 756 s, 720 s, 695 s, 644 s, 633 s, 600 m, 543 m, 519 m, 502 w, 393 w, 389 w. − EI MS (70 eV); *m/z* (%): 527 (4) [M$^+$], 293 (6) [$MeOC_6H_4C(NSiMe_3)_2^+$], 73 (100) [$SiMe_3^+$]. − $C_{23}H_{39}ClN_4OSi_2Ti$ (527.09): calcd. C 52.41, H 7.46, N 10.63; found C 52.53, H 7.66, N 10.21.

N-tert-Butylimidochloro[P,P-diphenylbis(N-trimethylsilylimino)-phosphinato](pyridine)titanium(IV) (**4**): Orange crystals, m.p. 145−147°C. Yield: 2.61 g (88%). − IR (cm^{-1}): ṽ = 2956 m, 2895 m, 1604 w, 1591 w, 1485 w, 1438 m, 1403 w, 1390 w, 1377 w, 1353 w, 1257 s, 1247 s, 1212 m, 1138 s, 1115 vs, 1105 vs, 1090 vs, 1070 s, 1044 m, 1028 w, 1014 w, 999 w, 841 vs, 786 s, 751 s, 724 s, 696 vs, 660 s, 640 m, 626 m, 586 s, 532 vs, 509 s, 428 m, 366 m, 321 s, 297 m, 280 s, 248 m, 214 m. − ^1H NMR (C_6D_6): δ = 8,86 (m, 1 H, p-C_5H_5N), 8,63 (m, 2 H, m-C_5H_5N), 8,16-7,97 (m, 6 H, m,p-C_6H_5), 7,06 (m, 2 H, o-C_5H_5N), 1,52 (s, 9 H, *t*Bu), 0,33 (s, 9 H, $SiMe_3$), 0,10 (s, 9 H, $SiMe_3$). − EI MS (70 eV); *m/z* (%): 593 (2) $[M^+]$, 578 (3) $[M^+ - CH_3]$, 345 (100) $[Ph_2PN(SiMe_3)_2^{\cdot+}]$, 73 (78) $[SiMe_3^{\cdot+}]$. − $C_{27}H_{42}ClN_4PSi_2Ti$ (593.14): calcd. C 54.68, H 7.14, N 9.45; found C 54.01, H 7.29, N 9.37.

Bis(pyridine)lithium P,P-Diphenylbis(N-trimethylsilylimino)-phosphinate (**5**): This compound was isolated as a by-product during the preparation of **4** and isolated as pale yellow crystals by fractional crystallization from hexane. All spectroscopic data (IR, ^1H NMR, ^{31}P NMR) were in good agreement with those of an authentic sample prepared directly by addition of pyridine to a hexane solution of $Li[Ph_2P(NSiMe_3)_2]$.[51] − $C_{28}H_{38}LiN_4PSi_2$ (524.72): calcd. C 64.04, H 7.30, N 10.68; found C 64.11, H 7.44, N 10.03.

N-tert-Butylimidobis[N,N-bis(isopropyl)benzamidinato](pyridine)titanium(IV) (**6**): Ochre, microcrystalline solid, m.p. 138−139°C. Yield: 1.45 g (48%). − IR (cm^{-1}): ṽ = 2964 s, 2920 s, 2890 s, 2862 s, 1645 m, 1635 m, 1616 w, 1600 s, 1576 m, 1523 s, 1505 s, 1480 s, 1441 s, 1386 s, 1372 s, 1345 s, 1336 s, 1243 s, 1221 s, 1213 s, 1203 s, 1168 s, 1135 s, 1120 s, 1112 s, 1070 s, 1039 s, 1030 (sh) m, 1007 vs, 949 m, 915 m, 798 m, 782 s, 757 s, 737 m, 701 vs, 631 m, 583 m, 525 s, 432 m, 300 m, 295 (sh) m, 282 m, 277 (sh) m. − ^1H NMR (C_6D_6): δ 7.34−7.06 (m, 10 H, C_6H_5), 3.58−3.35 (m, 4 H, *i*Pr-CH), 1.58−1.26 (m, 24 H, *i*Pr-CH_3), 1.01 (s, 9 H, *t*Bu). − $C_{35}H_{52}N_6Ti$ (604.72): calcd. C 69.52, H 8.67, N 13.90; found C 69.58, H 8.79, N 14.12.

N-tert-Butylimidobis[P,P-diphenylbis(N-trimethylsilylimino)-phosphinato]titanium(IV) (**7**): Red crystals, m.p. 130−132°C. Yield: 1.72 g (41%). − IR (cm^{-1}): ṽ = 3077 w, 3055 m, 2953 s, 2912 m, 2897 m, 1591 w, 1484 w, 1436 s, 1407 m, 1351 m, 1313 m, 1245 vs, 1209 m, 1181 w, 1153 (sh) m, 1115 vs, 1095 s, 1067 s, 1028 m, 999 w, 933 m, 840 vs, 770 s, 747 s, 731 s, 716 s, 695 s, 663 s, 655 (sh) s, 623 m, 615 m, 595 m, 529 s, 506 m, 489 m, 448 m, 409 m, 261 m, 239 m. − ^1H NMR (C_6D_6): δ 8.86 (m, 2 H, m-C_5H_5N), 8.65 (m, 1 H, p-C_5H_5N), 8.16−7.96 (m, 6 H, m,p-C_6H_5), 7.07 (m, 4 H, o-C_6H_5), 6.56 (m, 2 H, o-C_5H_5N), 1.52 (s, 9 H, *t*Bu), 0.33 (s, 9 H, $SiMe_3$), 0.10 (s, 9 H, $SiMe_3$). − $C_{40}H_{65}N_5P_2Si_4Ti$ (838.16): calcd. C 57.32, H 7.82, N 8.36; found C 57.42, H 8.04, N 8.30.

Crystal Structure Determination of **7**: $C_{40}H_{65}N_5P_2Si_4Ti$ (838.17), monoclinic, space group, a = 11.198(15), b = 22.055(26), c = 18.842(23) pm, β = 96.65(10)°, V = 4.6221(10) nm^3, Z = 4, d = 1.204 Mg/m^3, μ = 3.465 mm^{-1}, F(000) = 1792, crystal dimensions: 0.60 × 0.40 × 0.40 mm, 2θ range: 4−60°, number of measured reflexions: 6861 (5533 observed with $F^2 > 2\sigma F^2$), refined parameters: 487, goodness of fit: 1.058, R = 0.0772, wR = 0.1983. Further details of the crystal structure determination may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-380139, the names of the authors, and the journal citation.

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