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Synthesis and Structure of Trialkyltantalum Complexes Stabilized by Aminopyridinato Ligands

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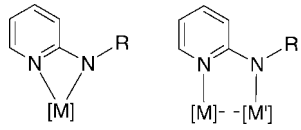
(4-Methylpyridin-2-yl)(trimethylsilyl)amine (**1**), (6-methylpyridin-2-yl)(trimethylsilyl)amine (**2**), and (2,6-diisopropylphenyl)(pyridin-2-yl)amine (**3**) were deprotonated and used as ligands to synthesize trialkyltantalum complexes. The reaction of 2 equiv. of **1** or **2** with pentabenzyltantalum afforded tribenzyltantalum(V) complexes by toluene elimination. Analogous reaction using **3** failed. Lithiation of **3** followed by the reaction with tribenzyltantalum dichloride gave rise to the corresponding tribenzyl complex. Other alkyltantalum complexes stabilized by this ligand environment can be prepared by treating tantalum pentachloride with 2 equiv. of lithiated **3** to form a bis(aminopyridinato)tantalum trichloride. The reaction of this trichloride with 3 equiv. of alkyllithium compounds like methyllithium affords the corresponding trialkyltantalum complexes. X-ray diffraction studies of four of the synthesized complexes were carried out. They adopt two different coordination environments, either slightly distorted capped octahedrons (sterically less demanding aminopyridinato ligands) or pentagonal bipyramids (bulkier aminopyridinato ligands). The alkyl species were surprisingly stable at elevated temperatures and no formation of mixed alkyl/alkylidene complexes was observed. Alkyl cation formation and the behaviour of a selection of these compounds in olefin polymerization were explored.

Introduction

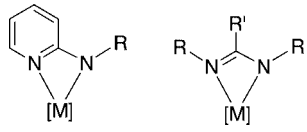
Aminopyridinato ligands[1] are interesting amido ligands because of the flexibility of their binding mode and the ligand "asymmetry". The dominating binding mode in early transition metal and lanthanide chemistry[2] is the strained η^2 coordination (Scheme 1, left). The bridging binding mode (Scheme 1, right) is characteristic for late transition metal complexes. Of course, there are exceptions like homoleptic strained η^2-bound (aminopyridinato)palladium complexes.[3] The ligand "asymmetry" caused by the two different donor functionalities−the pyridine and amido function−might be considered as an additional interesting feature especially in comparison to the closest "relatives", the amidinates.[4]

Group 5 metal complexes stabilized by aminopyridinato ligands (Scheme 2, left) have been investigated to a lesser extent than related amidinate[5] complexes (Scheme 2, right).

The first Ap (Ap = aminopyridinato) group 5 metal complex was published by Gambarotta 15 years ago.[6] A more detailed investigation of some aspects of the coordination chemistry of these ligands was started by Polamo. He applied the "direct synthesis" method to prepare a variety of niobium and tantalum complexes stabilized by aminopyridinato ligands.[7–10] Interesting examples of aminopyridinato low oxidation state group 5 metal complexes have been described by Gambarotta and Cotton.[11] Reactivity studies employing organometallic species are still very rare.[12,13] Because of this lack of information we became interested in alkyltantalum complexes. We also expect an easy access into this chemistry because of the recently published Kol synthesis of $[Ta(CH_2C_6H_5)_5]$.[14,15] We report here on the synthesis and structure of organotantalum complexes stabilized by aminopyridinato ligands. The formation of organ-



Scheme 1. Important binding modes of deprotonated 2-aminopyridines ([M] and [M′] = transition metal moiety; R = aryl, silyl, or alkyl substituent).



Scheme 2. Aminopyridinato (left) and amidinate (right) ligands ([M] = group 5 metal complex moiety; R, R′ = substituent).

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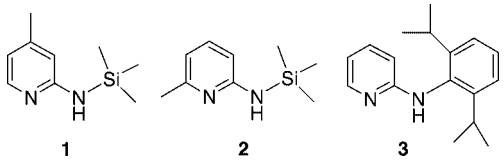
ocations and the relevance to olefin polymerization of a selection of these species is also discussed.

Results and Discussion

Synthesis of Ligands

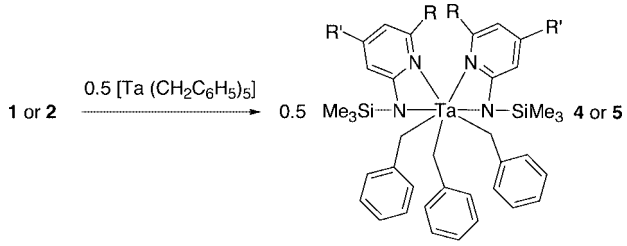
Compounds **1** and **2** were prepared as reported.[16,17] The aminopyridine **3** can be synthesized by palladium-catalyzed arylamination.[18] The reaction of 2-bromopyridine with 2,6-diisopropylaniline and sodium *tert*-butoxide in the presence of a Pd catalyst in toluene (90 °C, 48 h) leads after workup and purification by crystallization to compound **3** (Scheme 3) in good yield (70%).



Scheme 3. Applied aminopyridines.

Synthesis and Structure of Tantalum Complexes

Reaction of 2 equiv. of **1** with $[Ta(CH_2C_6H_5)_5]$ in hexane at 60 °C results in the formation of **4** by toluene elimination (Scheme 4). No formation of benzylidene functionalities is observed by NMR spectroscopy in the course of this reaction. Complex **4** was isolated after workup in hexane in moderate yield as a yellow crystalline material.



Scheme 4. Synthesis of **4** and **5** (**4**: R = H, R′ = CH_3; **5**: R = H, R′ = CH_3).

The three benzyl groups show a broad doublet at δ = 2.96 ppm at room temperature indicative of a fast ligand exchange. Crystals suitable for X-ray analysis were grown from a hexane solution. Details of the X-ray crystal structure analysis are summarized in Table 3. The molecular structure of **4** is shown in Figure 1. The coordination of **4** is best described as a distorted capped octahedron. The methylene carbon atom of one of the benzyl ligands (C15) as well as the two pyridine nitrogen atoms occupy the first triangle and C8 as well as the two amido nitrogen atoms the second triangle. In order to apply a slightly increased steric bulk in close proximity to the metal center 2 equiv. of **2** were treated with $[Ta(CH_2C_6H_5)_5]$ under the same conditions as applied to **4**. The resulting benzyl complex **5** was obtained in moderate yield (Scheme 4). The three benzyl groups give two doublets at δ = 2.98 and 3.18 ppm. The product was characterized by X-ray analysis (molecular structure is shown in Figure 2) in addition to NMR spectroscopy. Details of the X-ray crystal structure analysis are summarized in Table 3. The coordination of **5** is best described as a capped octahedron (first triangle N1, N2, and N4; second triangle N3, C15, and C22). In both cases, the rigid aminopyridinato ligands induce distortion from the ideal symmetry. The Ta–C bond lengths lay in the ranges of 2.247–2.318 Å and 2.248–2.264 Å, respectively, for **4** and **5**, which clearly indicate η^1 binding of all benzyl groups in the solid state.

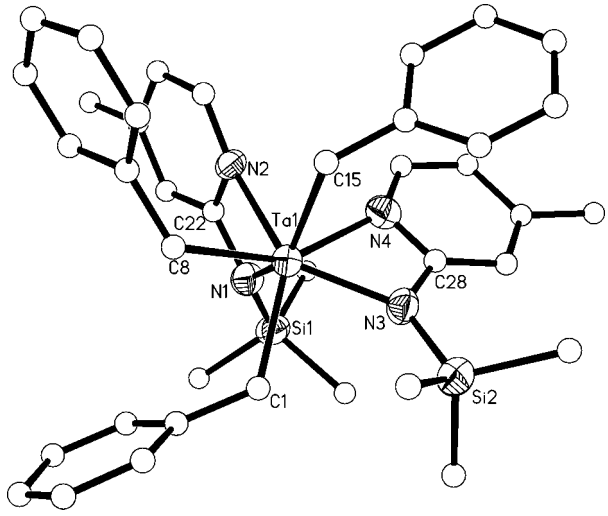


Figure 1. Molecular structure of **4**; selected bond lengths [Å] and angles [°]: Ta–C1 2.248(9), Ta–N4 2.230(8), Ta–N2 2.266(8), Ta–N1 2.123(10), Ta–N3 2.132(8), Ta–C8 2.264(1), Ta–C15 2.257(10), N2–C22 1.332(13), N1–C22 1.400(13), N3–C28 1.376(13); N1–Ta–N2 61.00(3), N1–C22–N2 109.49(8), Ta–N2–C22 92.05(6), Ta–N1–C22 96.31(6), N4–Ta–N3 59.10(3), N3–C28–N4 109.06(8), Ta–N3–C28 96.53(6), Ta–N4–C28 93.21(6), C1–Ta–C8 78.28(4), C15–Ta–C8 78.60(4), C1–Ta–C15 126.83(4).

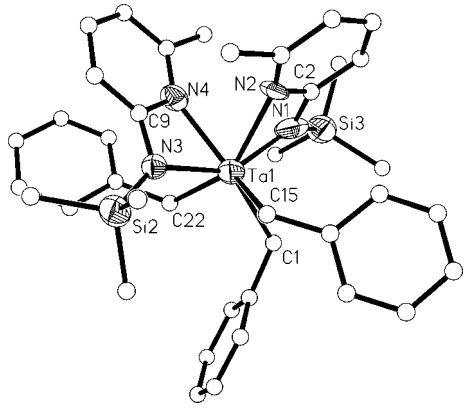
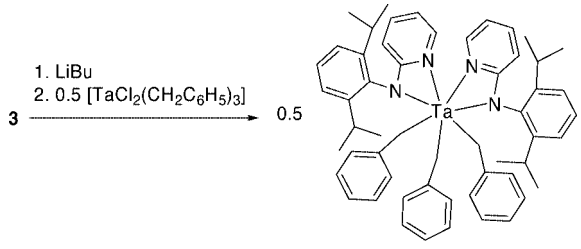


Figure 2. Molecular structure of **5**; selected bond lengths [Å] and angles [°]: Ta–C1 2.250(11), Ta–N2 2.382(10), Ta–N4 2.248(10), Ta–N1 2.069(11), Ta–N3 2.212(9), Ta–C15 2.247(11), Ta–C22 2.318(10), N2–C2 1.379(16), N4–C9 1.355(14), N1–C2 1.375(15), N3–C9 1.391(13); C1–Ta–C15 81.09(5), C1–Ta–C22 76.15(4), C15–Ta–C22 130.18(5), N1–Ta–N2 60.31(4), N1–C2–N2 109.77(12), Ta–N1–C2 101.02(8), Ta–N2–C2 87.22(9), N4–Ta–N3 61.44(3), Ta–N3–C9 93.36(7), Ta–N4–C9 92.80(7), N4–C9–N3 112.12(11).

In order to increase the steric bulk of the used aminopyridinato ligands drastically we introduced the 2,6-diisopropylphenyl substituent at the amido nitrogen atom instead of the $SiMe_3$ group. Application of the toluene elimination route starting from $[Ta(CH_2C_6H_5)_5]$ was not successful and salt metathesis was adopted. The reaction of 2 equiv. of the lithium salt of **3** with $[TaCl_2(CH_2C_6H_5)_3]$[14] at room temperature (Scheme 5) resulted in the formation of the tribenzyl complex **6**. The ^1H NMR spectra of this compound shows two different sets of signals for benzyl protons. One signal corresponds to four methylene protons of the benzyl substituents and the other to the remaining two. We propose a pentagonal-bipyramidal arrangement in solution with the two amino and one of the benzyl moieties in the equatorial plane. Because of the steric bulk of the deprotonated **3** no exchange on the NMR time scale at room temperature is observed. Two benzyl resonances were found, one at δ = 3.60 ppm and the second at δ = 2.79 ppm.

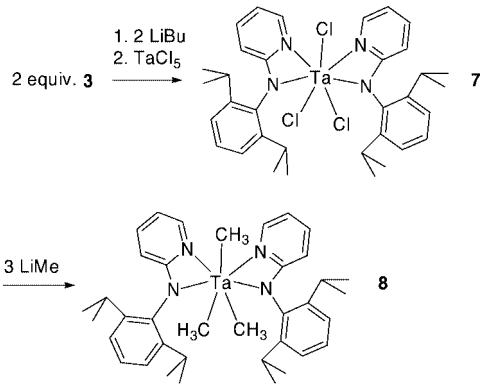


6

Scheme 5. Synthesis of **6**.

The first Schrock-type alkylidene complex, $[Ta(CH_2tBu)_3(CHtBu)]$, was prepared in 1974.[19] Various mono- and polydentate ligand systems that support this functionality have been introduced in recent years and several synthetic methodologies are known that lead to the alkylidene complexes like, for instance, an α-elimination reaction sequence from dialkyl precursors.[20] However, the complexes **4**, **5**, and **6** do not form mixed benzyl/benzylidene complexes neither during the synthesis nor by treatment of the trialkyltantalum complexes at elevated temperatures (80 °C). In order to prepare other trialkyltantalum complexes supported by deprotonated **3** — the sterically most demanding of the three ligands described in this publication — we synthesized the corresponding tantalum trichloride species **7** (Scheme 6).

Compound **7** can be synthesized by the reaction of **3** with $TaCl_5$ (Polamo method "direct synthesis"[7]). Because of a relatively low yield using this "direct synthesis" salt metathesis (Scheme 6) was applied and gave rise to **7** in better yield. The success of salt metathesis using lithiated **3** and $TaCl_5$ is in contrast to Polamo's observations. He developed his method due to problems with the salt metathesis approach in similar reactions. The trimethyltantalum complex **8** results when 3 equiv. of LiMe were treated with **7**. The X-ray crystal structures of **7** (Figure 3) and **8** (Figure 4) revealed a distorted pentagonal-bipyramidal coordination. In **7** the two chloro ligands occupy the axial positions of the polyhedra and the two pairs of nitrogen and the third chloride ion form the pentagonal (equatorial) plane. In **8** methyl ligands adopt the same coordination sites as the chloro ligands in **7**. A distortion is caused by the small N–Ta–N angles due to the strained binding mode of the aminopyridinato ligands. In **7** they are 60.1(3) and 60.4(3)° and in **8** 59.25(2)°. Both lead to a situation in which all other angles in the pentagonal plane are over 72°. In **7** N–Ta–Cl(2) *cis* angles are 77.9(2) and 77.3(2)° and in **8** the N–Ta–C(1) *cis* angles are 77.43(10)°. N–Ta–N angles involving the amido bonds of the aminopyridinato ligands are the widest, 84.4(3)° in **7** and 86.65(18)° in **8**. The Cl_{ax}-Ta–Cl_{eq} angles for **7** are 99.87(9)° and 99.64(9)° and the C_{ax}-Ta–C_{eq} angles for **8** are 94.02(15)° and 93.23(16)°. Details of the X-ray crystal structure analyses of **7** and **8** are summarized in Table 3. The ^1H NMR spectrum shows two different sets of signals for methyl protons. The two methyl groups present above and below the pentagonal plane (axial positions) show a resonance at δ = 1.26 ppm and the in-plane methyl ligand at δ = 0.63 ppm. Similar observations have been made for **6**. The trimethyl complex **8** was found to be stable



Scheme 6. Synthesis of **7** and **8**.

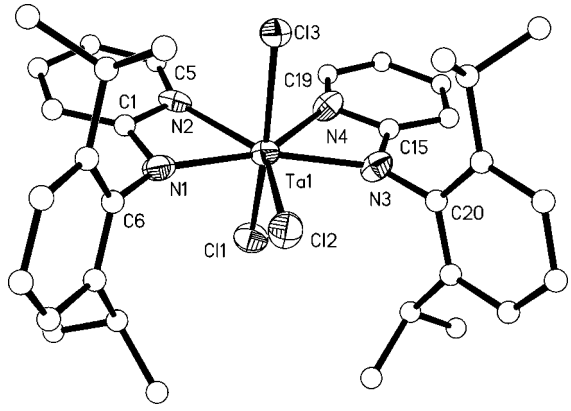


Figure 3. Molecular structure of **7**; selected bond lengths [Å] and angles [°]: C1–N2 1.339(11), C1–N1 1.376(11), C5–N2 1.337(11), C6–N1 1.438(11), C15–N3 1.391(10), C15–N4 1.352(12), C19–N4 1.337(11), C20–N3 1.422(11), N1–Ta1 2.072(8), N2–Ta1 2.264(8), N3–Ta1 2.098(7), N4–Ta1 2.263(7), Cl1–Ta1 2.352(2), Cl2–Ta1 2.349(2), Cl3–Ta1 2.376(2); C1–N1–Ta 100.45(6), C1–N2–Ta 92.92(5), C1–N2–C5 118.55(8), C15–N4–C19 118.13(8), C15–N3–Ta 99.66(6), C15–N4–Ta 93.42(5), N1–Ta–N2 60.05(3), N3–Ta–N4 60.38(3), N2–C1–N1 106.52(8), N4–C15–N3 106.53(8), Cl1–Ta–Cl3 160.49(8), Cl1–Ta–Cl2 99.87(9), Cl2–Ta–Cl3 99.63(9).

towards elevated temperatures in terms of the formation of mixed methyl/methylidene species. Heating of **8** in toluene at 80 °C for 40 min did not affect the structure of the compound. When harsher conditions were employed, i.e., heating to 120 °C for 30 min, **8** started to decompose slowly without any signs of methylidene formation.

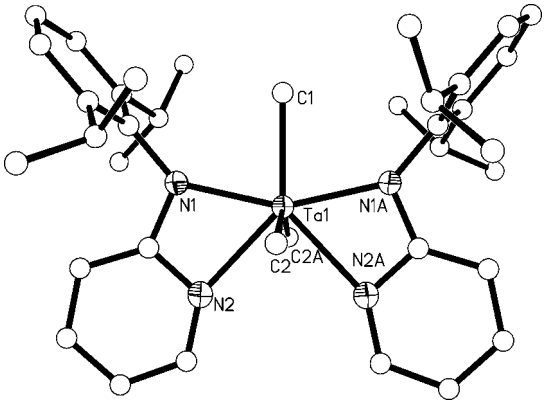
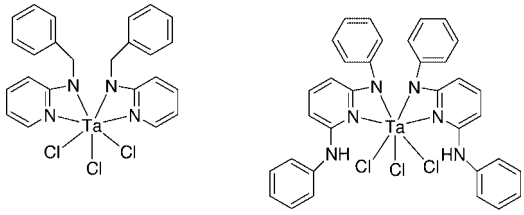


Figure 4. Molecular structure of **8**; selected bond lengths [Å] and angles [°]: C1–Ta1 2.190(6), C2–Ta1 2.203(4), N1–Ta1 2.105(3), N2–Ta1 2.332(4), N1–Ta1–N1A 154.86(19), C1–Ta1–C2 106.89(12), N1–Ta1–C2 93.23(16), C2A–Ta(1)–C2 146.2(2), N1–Ta1–N2 145.88(13), N1–Ta1–N2 59.25(13), C1–Ta1–N2 136.67(9), C2–Ta1–N2 77.25(16), N2–Ta1–N2A 86.65(18).

Formation of Organocations and Their Application in Ethylene Polymerization

Because of the high ethylene polymerization activity observed for the tantalum complexes **9** and **10**[12] (Scheme 7) we became interested in exploring the polymerization behavior of some of the complexes discussed in this study.



Scheme 7. Structures of **9** and **10**.

Ethylene polymerization studies were performed using **7** (Table 1) and **8** (Table 2) as pre-catalysts.

Table 1. Ethylene polymerization results, activation of **7** using PMAO [PMAO = polymethylaluminoxane $(AlOMe)_x$].[a]

Pre-cat. [μmol]	PMAO [mmol]	PE [g]	Activity [kg(PE)mol(Ta)$^{-1}$h^{-1}bar^{-1}]
10	5	0.2	16

[a] 260 mL of toluene as solvent, 5 bar of ethene, 50 °C, 15 min run time, Ta/Al = 1:500 (m/m).

Ethylene polymerization activity of **7** after activation with PMAO is low. This is in contrast to what was observed for **9** and **10**. Thus, we expected to see a significantly better catalyst performance when starting from the methyl complex **8** and activating with trialkylammonium tetrakis(pentafluorophenyl)borate. No significant improvement in terms of activity was found by changing the activation procedure. Because of the low activity no molecular weight analysis of the polymers was accomplished. The generation of cationic complexes was studied in an NMR scale reaction. Reaction of **8** with 1 equiv. of $B(C_6F_5)_3$ in CD_2Cl_2 results in the abstraction of one of the axial methyl groups. A new resonance at δ = 1.86 ppm was observed for this methyl group in the ^{1}H NMR spectra. The resulting organocation is not stable in solution and decomposes rapidly into unidentified species.

Table 2. Ethylene polymerization results, activation of **8** using trialkylammonium tetrakis(pentafluorophenyl)borate.[a]

Run no.	Pre-cat. [μmol]	$B(C_6F_5)_4^-$ [μmol]	TIBAO [mmol]	PE [g]	Activity [kg(PE)mol(Ta)$^{-1}$h^{-1}bar^{-1}]
1	–	11	0.1	0.05	–
2	10	11	0.1	0.06	5
3	10	22	0.1	0.16	13

[a] 260 mL of toluene as solvent, 5 bar of ethene, 80 °C, 15 min run time, Ta/Al = 1:20 (m/m); TIBAO = tetraisobutylaluminoxane ($[iBu_2Al]_2O$).

Conclusions

Trialkyltantalum complexes stabilized by aminopyridinato ligands can be synthesized by salt metathesis or toluene elimination. They adopt the coordination of either a capped octahedron or a pentagonal bipyramid depending on the steric demand of the aminopyridinato ligand. These trialkyltantalum complexes are thermally unusually stable towards α-H elimination. They form rather unstable organocations and the instability of these cations might be the reason for the low activity in ethylene polymerization.

Experimental Section

General Procedures

Synthesis and Structure Analysis: All manipulations were performed with rigorous exclusion of oxygen and moisture in Schlenk-type glassware on a dual manifold Schlenk line or in an argon-filled glove box (mBraun 120-G) with a high-capacity recirculator (<0.1 ppm O_2). Non-halogenated solvents were dried by distillation from sodium wire/benzophenone. Commercial $TaCl_5$ (Lancaster) was used as received. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were degassed, dried, and distilled prior to use. NMR spectra were recorded with a Bruker ARX at 250 MHz and chemical shifts are reported in ppm relative to the deuterated solvent. Elemental analyses (CHN) were carried out using a Vario EL III instrument. X-ray crystal structure analyses were performed by using a STOE-IPDS II diffractometer equipped with an Oxford Cryostream low-temperature unit. Crystal structure data are presented in Table 3. Structure solution and refinement was accomplished using SIR97,[21] SHELXL97,[22] and WinGX.[23] CCDC-297697 (**4**), -297698 (**5**), -297699 (**7**), and -297700 (**8**) contain the supplementary crystallographic data for

Table 3. Details of the X-ray crystal structure analyses.

Compound	**4**	**5**	**7**	**8**
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	*C*2/*c*	$P2_1/n$	$P\bar{1}$	*C*2/*c*
a [Å]	23.279(3)	13.955(3)	10.3627(9)	14.1240(10)
b [Å]	18.761(2)	14.704(3)	19.7101(18)	12.5620(10)
c [Å]	20.204(3)	18.617(3)	21.343(2)	22.694(2)
α [°]	90	90	96.120(7)	90
β [°]	117.557(8)	91.680(2)	103.540(7)	93.375(5)
γ [°]	90	90	90.410(7)	90
V [Å^3]	7823(3)	3818(2)	4211.6(7)	4019.5(6)
Crystal size [mm]	0.12 × 0.1 × 0.08	0.12 × 0.11 × 0.06	0.16 × 0.1 × 0.05	0.99 × 0.34 × 0.44
$\rho_{calcd.}$ [g cm^{-3}]	1.381	1.414	1.434	1.333
μ [mm^{-1}] (Mo-K_α)	0.7107	0.7107	0.7107	0.7107
T [K]	193(2)	193(2)	193(2)	193(2)
θ range [°]	1.47–26.19	1.77–26.21	1.35–25.83	1.80–25.68
No. of unique refl.	7732	7506	15909	3604
No. of obsd. refl. [$I > 2\sigma(I)$]	4508	2470	9228	3508
No. of parameters	415	409	880	214
wR_2 (all data)	0.1282	0.1033	0.1018	0.0924
R value [$I > 2\sigma(I)$]	0.0755	0.0542	0.0632	0.0312

this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Polymerization: Toluene (Aldrich, anhydrous, 99.8%) was passed through columns of Al_2O_3 (Fluka), BASF R3-11 supported Cu oxygen scavenger, and molecular sieves (4 Å, Aldrich). Ethylene (AGA polymer grade) was passed over BASF R3-11 supported Cu oxygen scavenger and molecular sieves (4 Å, Aldrich). PMAO (4.9 wt.-% Al in toluene, Akzo Nobel), *N*,*N*,*N*-trialkylammonium tetrakis(pentafluorophenyl)borate [6.2 wt.-% $B(C_6F_5)_4^-$ in Isopar, DOW Chemicals], and TIBA (Witco) were used as received. TIBAO was prepared according to published procedures.[24]

Synthesis of 3:[25] Toluene (25 mL) was added to a Schlenk vessel charged with tris(dibenzylideneacetone)dipalladium (0.082 g, 0.09 mmol), NaO*t*Bu (0.750 g, 7.8 mmol), and 1,3-bis(diphenylphosphanyl)propane (0.074 g, 0.18 mmol). To the resulting suspension 2-bromopyridine (0.57 mL, 6 mmol) and 2,6-diisopropylaniline (1.47 mL, 7.8 mmol) was added. The solution was stirred and heated to 90 °C for 48 h. On cooling to room temperature, water and diethyl ether were added to the resulting red solution. The organic phase was extracted and the remaining inorganic phase was further washed with diethyl ether (3 × 20 mL). The combined organic phases were washed with a saturated sodium chloride solution and dried with sodium sulfate. The solvent was removed under reduced pressure and the resulting reddish solid was purified using silica gel chromatography (eluent: dichloromethane). The solvent was removed under reduced pressure and the product was recrystallized from pentane as a white crystalline material. Yield 1.07 g (70%). $C_{17}H_{22}N_2$ (254.37): calcd. C 80.27, H 8.72, N 11.01; found C 80.30, H 8.75, N 10.82. ^{1}H NMR (C_6D_6, 298 K): δ = 1.10 [d, 12 H, $CH(CH_3)_2$], 3.39 [sept, 2 H, $CH(CH_3)_2$], 5.88 (d, 1 H, Py-3-H), 6.20 (dd, 1 H, Py-5-H), 6.89 (t, 1 H, Py-4-H), 7.17–7.29 (m, 3 H, Ar-CH), 7.99 (dd, 1 H, Py-6-H), 8.34 (br. s, 1 H, NH) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 23.98 [4 CH_3, $CH(CH_3)_2$], 28.67 [2 CH, $CH(CH_3)_2$], 105.62 (CH, Py-C-5), 112.94 (CH, Py-C-3), 124.22 (2 CH, Ar-C-9,11), 134.69 (CH, Py-C-4), 137.68 (2 CH, Ar-C-8,12), 148.45 (1 C, Ar-C-7), 148.57 (1 CH, Py-C-6), 160.51 (1 CH, Py-C-2) ppm.

Synthesis of 4: Compound **1** (0.380 g, 2 mmol, 425 μL) in hexane (5 mL) was added slowly to a stirred solution of $[Ta(CH_2C_6H_5)_5]$ (0.636 g, 1 mmol) in hexane (15 mL) at –33 °C. The mixture was warmed to room temperature and was further heated at 60 °C for 2 h as a color change was observed from brown to deep red. The mixture was filtered and the volume of the solvent was reduced in vacuo. The solution was cooled at –25 °C overnight to afford a yellow crystalline material. Yield 0.365 g (43%). $C_{39}H_{51}N_4Si_2Ta$ (812.97): calcd. C 57.62, H 6.32, N 6.89; found C 57.36, H 6.62, N 6.29. ^{1}H NMR (C_6D_6, 298 K): δ = 0.40 [s, 18 H, $Si(CH_3)_3$], 1.61 (s, 6 H, CH_3), 2.96 (br. d, 6 H, CH_2), 5.76 (d, 2 H, Py-5-H), 5.88 (s, 2 H, Py-3-H), 6.74 (t, 3 H, Ar-4-H), 6.89–7.10 (m, 14 H, Py-6-H, Ar-2, 3, 5, 6 H) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 2.45 (6 C, 6 CH_3), 21.6 (2 C, 2 CH_3), 99.40 (br. and flat s, 3 CH_2), 111.87 (2 CH, Py-C-3/5), 114.05 (2 CH, Py-C-3/5), 122.49 (3 CH, Benz-C-4), 126.83 (6 CH, Benz-C-3,5), 128.20 (6 CH, Benz-C-2,6), 141.51 (3 C, Benz-C-1), 151.53 (2 C, Py-C-4), 153.26 (2 CH, Py-C-6), 164.91 (2 C, Py-C-2) ppm.

Synthesis of 5: Compound **2** (0.463 g, 2.57 mmol, 546 μL) in hexane (5 mL) was added slowly to a stirred solution of $[Ta(CH_2C_6H_5)_5]$ (0.817 g, 1.28 mmol) in hexane (15 mL) at –33 °C. The mixture was warmed to room temperature and further heated at 60 °C for 2 h. The mixture was filtered and the volume of the solvent was reduced in vacuo. The solution was cooled at –25 °C overnight to afford a yellow crystalline material. Yield 0.460 g (44%). $C_{39}H_{51}N_4Si_2Ta$ (812.97): calcd. C 57.62, H 6.32, N 6.89; found C 56.73, H 6.24, N 6.54. ^{1}H NMR (C_6D_6, 298 K): δ = 0.27 [s, 18 H, $Si(CH_3)_3$], 1.92 (s, 6 H, CH_3), 3.15–2.96 (2 d, 6 H, CH_2), 5.65 (d, 2 H, Py-5-H), 5.83 (d, 2 H, Py-3-H), 6.69 (dd, 6 H, Benz-2,6-H), 7.00 (t, 6 H, Benz-3,5-H), 7.44 (t, 2 H, Py-4-H) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 2.57 (6 C, 6 CH_3), 21.56 (2 C, 2 CH_3), 100.34 (3 CH_2), 108.34 (2 CH, Py-C-3/5), 113.95 (2 CH, Py-C-3/5), 122.66 (3 CH, Benz-C-4), 126.67 (6 CH, Benz-C-3,5), 129.42 (6 CH, Benz-C-2,6), 138.32 (3 C, Benz-C-1), 151.97 (2 CH, Py-C-4), 153.17 (2 C, Py-C-6), 161.49 (2 C, Py-C-2) ppm.

Synthesis of 6: To a stirred solution of **3** (0.557 g, 2.14 mmol) in diethyl ether (10 mL), *n*BuLi (1.34 mL, 1.6 M, 2.14 mmol) was added at 0 °C. This "ligand solution" was warmed slowly to room temperature and stirred for 2 h. This solution was slowly added to $[TaCl_2(CH_2C_6H_5)_3]$ (0.562 g, 1.07 mmol) in hexane (10 mL) at room temperature. The mixture was stirred overnight and a color change from red to dark brown was observed. LiCl was filtered off

and the volume of the solvent was reduced in vacuo. The solution was cooled at –25 °C overnight to afford an orange crystalline material. Yield 0.564 g (55%). $C_{55}H_{63}N_4Ta$ (961.06): calcd. C 68.74, H 6.61, N 5.83; found C 67.44, H 6.64, N 5.51. ^{1}H NMR (C_6D_6, 298 K): δ = 1.15–1.27 [dd, 24 H, 2 $CH(CH_3)_2$], 2.79 (s, 2 H, CH_2), 3.60 (s, 4 H, 2 CH_2), 3.85 [sept, 4 H, 4 $CH(CH_3)_2$], 5.52 (d, 2 H, Py-3-H), 5.81 (t, 2 H, Py-5-H), 6.22 (d, 4 H, Ar-H), 6.27 (d, 2 H, Py-4-H), 6.62 (dd, 2 H, Py-6-H), 6.78–6.67 (m, 5 H, Ar-H), 6.94–6.86 (m, 6 H, Ar-H), 7.19–7.16 (m, 6 H, Ar-CH) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 23.22 [8 CH_3, $CH(CH_3)_2$], 26.28 [2 CH, $CH(CH_3)_2$], 28.80 [2 CH, $CH(CH_3)_2$], 83.50 (3 C, CH_2), 106.53 (2 CH, Py-C-3/5), 112.39 (2 CH, Py-C-3/5), 123.18 (4 CH, Ar-C-9,11), 125.31 (6 CH, Benz-C-3,5), 126.57 (6 CH, Benz-C-2,6), 127.09 (3 CH, Benz-C-4), 129.96 (4 CH, Ar-C-8,12), 139.55 (2 CH, Ar-C-10), 141.87 (2 CH, Py-C-4), 143.08 (2 C, Ar-C-7), 146.36 (3 C, Benz-C-1), 148.46 (2 CH, Py-C-6), 169.21 (2 CH, Py-C-2) ppm.

Synthesis of 7. Method I: $TaCl_5$ (1.432 g, 4 mmol) and **3** (2.035 g, 8 mmol) were heated at 110 °C. The melt started to turn dark brown immediately. During the reaction gas formation was observed. After 1 h, toluene (30 mL) was added and the dark-red reaction mixture was further refluxed for 2 h. The solution was filtered while hot and the volume was reduced until red crystals began to appear. The solution was cooled and a red crystalline material was obtained overnight. Yield 1.103 g (35%). $C_{34}H_{42}Cl_3N_4Ta$ + 0.5 C_7H_8 (840.10): calcd. C 53.61, H 5.51, N 6.67; found C 53.67, H5.54, N 6.08. ^{1}H NMR (C_6D_6, 298 K): δ = 1.13–1.48 [dd, 24 H, $CH(CH_3)_2$], 2.10 (s, 3 H, toluene) 3.86 [sept, 4 H, $CH(CH_3)_2$], 5.74 (d, 2 H, Py-3-H), 6.05 (t, 2 H, Py-5-H), 6.83 (t, 2 H, Py-4-H), 7.28–7.16 (m, 6 H, Ar-H), 8.06 (d, 2 H, Py-6-H) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 24.73 [4 CH_3, $CH(CH_3)_2$], 24.95 [4 CH_3, $CH(CH_3)_2$], 28.22 [4 CH, $CH(CH_3)_2$], 107.56 (2 CH, Py-C-3/5), 113.50 (2 CH, Py-C-3/5), 124.46 (4 CH, Ar-C-9,11), 140.19 (2 CH, Ar-C-10), 140.66 (CH, Py-C-4), 141.15 (2 C, Ar-C-7), 147.37 (4 C, 2 CH, Ar-C-8,12, Py-C-6), 169.86 (2 C, Py-C-2) ppm. **Method II:** Lithiated **3** (1.041 g, 4 mmol) in diethyl ether (20 mL) was added to $TaCl_5$ (0.716 g, 2 mmol) in toluene (5 mL) at room temperature and the reaction mixture was stirred at room temperature overnight. The solution was filtered and the solvent was removed in vacuo. The red residue was washed with hexane (5 mL) and dried under vacuum. Yield 0.92 g (58%).

Synthesis of 8: LiMe (1.88 mL, 1.6 M, 3 mmol) was added to a stirred suspension of **7** (0.794 g, 1 mmol) in hexane (20 mL) at –40 °C. The red suspension was warmed to room temperature as the color started changing from red to yellow. The suspension was further stirred for 2 h. The brown solution was filtered and the residue washed with diethyl ether (5 mL). The volume was reduced in vacuo and the solution was cooled at –25 °C overnight to afford a yellow crystalline material. Yield 0.432 g (59%). $C_{37}H_{51}N_4Ta$ (732.78): calcd. C 60.65, H 7.02, N 7.65; found C 60.37, H 7.04, N 7.50. ^{1}H NMR (C_6D_6, 298 K): δ = 0.63 (s, 3 H, CH_3), 1.13 [d, 12 H, $CH(CH_3)_2$], 1.26 (s, 6 H, 2 CH_3),1.34 [d, 12 H, $CH(CH_3)_2$], 3.61 [sept, 4 H, $CH(CH_3)_2$], 5.54 (d, 2 H, Py-3-H), 6.18 (dd, 2 H, Py-5-H), 6.86 (t, 2 H, Py-4-H), 7.24–7.17 (m, 6 H, Ar-8,9,10-H) ppm.^{13}C NMR (C_6D_6, 298 K): δ = 24.10 [4 CH_3, $CH(CH_3)_2$], 24.18 [4 CH_3, $CH(CH_3)_2$], 25.10 (3 CH_3), 27.75 [2 CH, $CH(CH_3)_2$], 27.93 [2 CH, $CH(CH_3)_2$], 105.67 (2 CH, Py-C-3/5), 113.36 (1 CH, Py-C-3/5), 113.56 (1 CH, Py-C-5), 124.45 (4 CH, Ar-C-9,11), 127.09 (1 CH, Ar-C-10), 127.14 (1 CH, Ar-C-10), 138.91 (1 CH, Py-C-4), 139.11 (1 CH, Py-C-4), 141.32 (4 CH, Ar-C-8,12), 146.09 (4 CH, Py-C-6, 2 C, Ar-C-7), 168.32 (1 C, Py-C-2) ppm.

General Description of Polymerization Experiments: The catalytic ethylene polymerization reactions were performed in a stainless steel 1-L autoclave (Medimex) in semi-batch mode (ethylene was added by replenishing flow to keep the pressure constant). The reactor was temperature- and pressure-controlled and equipped with separated toluene, catalyst, and cocatalyst injection systems and a sample outlet for continuous reaction monitoring. At 5 bar of ethylene pressure multiple injection of the catalyst with a pneumatically operated catalyst-injection system was used. During a polymerization run the pressure, ethylene flow, inner and outer reactor temperature, and the stirrer speed were monitored continuously. In a typical semi-batch experiment, the autoclave was evacuated and heated at 125 °C for 1 h prior to use. The reactor was then brought to the desired temperature with stirring at 600 rpm and charged with 230 mL of toluene together with either the required amount of PMAO [2.76 g, Ta/Al = 1:500 (m/m)] or TIBAO scavenger [1 mL of a 0.1 M stock solution in toluene, Ta/Al = 1:20 (m/m)]. After pressurizing with ethylene to reach 5 bar total pressure the autoclave was equilibrated for 5 min. Subsequently 1 mL of a 0.01 M stock solution of the tantalum complex in toluene was injected together with 30 mL of toluene, to start the reaction. In the case where trialkylammonium tetrakis(pentafluorophenyl)borate was the activator, 1 mL of the tantalum complex stock solution and the appropriate amount of borate [0.12 g, Ta/B = 1:1.1 (m/m)] were premixed before injection. During the run the ethylene pressure was kept constant to within 0.2 bar of the initial pressure by replenishing flow. After the desired reaction time, the reactor was vented and the residual PMAO/TIBAO was destroyed by addition of 20 mL of ethanol. Polymeric product was collected, stirred in acidified ethanol for 30 min, and rinsed with ethanol and acetone on a glass frit. The polymer was initially dried in air and subsequently in vacuo at 80 °C.

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