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Acetylenetitanium Complex Stabilized by Aminopyridinato Ligands

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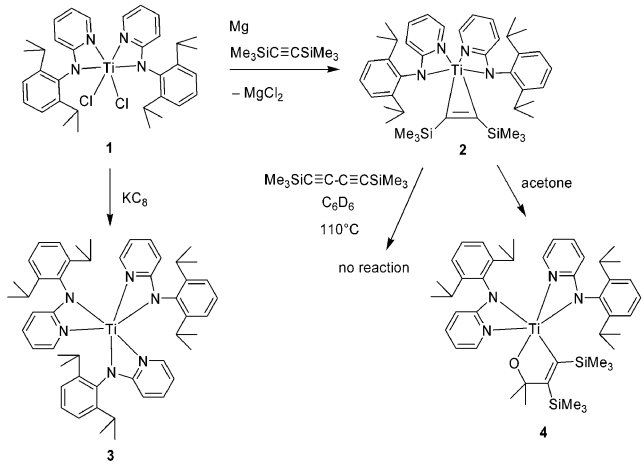
The first acetylenetitanium complex stabilized by aminopyridinato ligands has been prepared by the reaction of Ap_2TiCl_2 (**1**) – Ap-H = 2-[(2,6-diisopropylphenyl)amino]pyridine – with equimolar amount of bis(trimethylsilyl)acetylene in the presence of magnesium. The complex was characterized by spectroscopic methods as well as by X-ray single crystal structure analysis. Reduction of **1** with KC_8 under N_2 in the absence of any other stabilizing ligand leads to the ligand rearrangement product Ap_3Ti. In the reaction of the acetylenetitanium complex with acetone the titanaoxacyclopentene was formed.

Introduction

The stabilization of highly reactive low-valent early transition metal complexes is the key to rich and selective small-molecule activation chemistry of these compounds. A challenge is to generate these complexes as stable and easy to handle but nevertheless highly reactive compounds. One strategy is the protection of the reactive sites by an easily replaceable ligand. This strategy has been successfully applied to titanocenes and zirconocenes by using alkynes as a protecting ligand.[1] The chemistry of these complexes, and particularly their bonding situation, their spectroscopic properties, their reactivity and mechanistic behavior etc., has been described in several reviews.[1,2] Such complexes have been studied either using Cp (Cp = cyclopentadienyl) or variations of Cp ligands. However, using possible alternatives to Cp ligands to stabilize reduced group-4 metal centres have been investigated to a lesser extent.[3] In order to investigate such alternatives, we decided to employ aminopyridinato ligands. We have explored aminopyridinato ligands for many years[4] and only recently started to work with bulky versions of these ligands.[5] Herein we report on the synthesis and structure of a Cp-free acetylenetitanium complex and some preliminary reactivity studies of this compound.

Results and Discussion

The starting complex **1** (Scheme 1) was prepared in excellent yields by reacting two equivalents of 2-[(2,6-diisopropylphenyl)amino]pyridine[6] with $[(CH_3)_2NTiCl_3]$.[7] Crystals of **1** containing two toluene molecules per titanium atom were grown from concentrated toluene solution. The titanium centre has a distorted octahedral coordination (Figure 1). The Cl1–Ti–Cl2 angle [93.76(10)°] is close to the ideal value of 90° and smaller than in similar (aminopyridinato)chlorotitanium complexes [97.03(5)°[8] and 100.54(3)°[9]]. The first acetylene complex of titanocene without additional ligands was prepared by the reduction of $[Cp_2TiCl_2]$ with equimolar amounts of magnesium in the presence of tolane in THF.[10,11] We have found that this procedure can be used successfully to synthesize aminopyridinato-stabilized titanium complexes as well. The reaction of **1** with magnesium proceeds smoothly in the presence of bis(trimethylsilyl)acetylene at room temperature, affording the corresponding acetylene complex **2** in moderate yields (Scheme 1).



Scheme 1. Synthesis of **2**, **3**, and **4**.

Complex **2** was isolated as dark blue crystals and characterized by NMR spectroscopy. The structure was confirmed by X-ray diffraction studies.[12] The molecular structure of **2**

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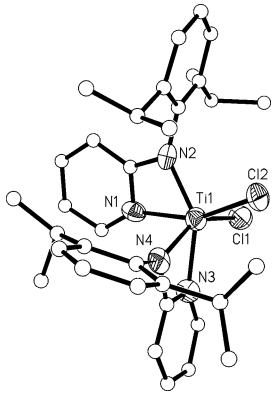


Figure 1. Molecular structure of 1 (ellipsoids correspond to the 50% probability level). Hydrogen atoms and two toluene molecules are omitted for clarity; selected bond lengths (Å) and angles (°): N1–Ti1 2.179(8), N2–Ti1 1.954(6), N3–Ti1 2.124(7), N4–Ti1 2.036(7), Cl1–Ti1 2.310(3), Cl2–Ti1 2.247(3); N4–Ti1–N3 63.2(3), N2–Ti1–N1 63.8(3), Cl2–Ti1–Cl1 93.76(10).

is shown in Figure 2. The small N–Ti–N angle [64.22(18)°] expresses the strained binding situation of the aminopyridinato ligands and the shorter N_{amido}–Ti [2.058(5) Å] distance compared to $N_{pyridine}$–Ti [2.152(5) Å] indicates the localization of the anionic function at the amido N-atom.[13] The carbon atoms of the acetylene, together with the silicon atoms bonded to them, form almost a planar system. The torsion angle SiC≡CSi is 2.0(2)°. The coordinated C≡C bond of the acetylene ligand [1.338(13) Å] is much longer than the normal C≡C bond (1.181 Å), its length being close to the value of 1.331 Å, typical for the C=C bond.[14] Furthermore, this value is significantly higher than that observed for [$Cp_2Ti(Me_3SiC{\equiv}CSiMe_3)$] [1.283(6) Å].[2c] The distances between the titanium atom and the carbon atoms of the coordinated alkyne are 2.090(7) Å which are slightly shorter than the values found for [$Cp_2Ti(Me_3SiC{\equiv}CSiMe_3)$] [2.136(5) and 2.139(4) Å]. The CCSi angles of 138.9(2)° differ from 180° to approach a value of 120°, typical of sp^2-hybridized carbon atoms and are smaller than what was found for the Cp stabilized complex [145.7(4) and 147.8(4)°].

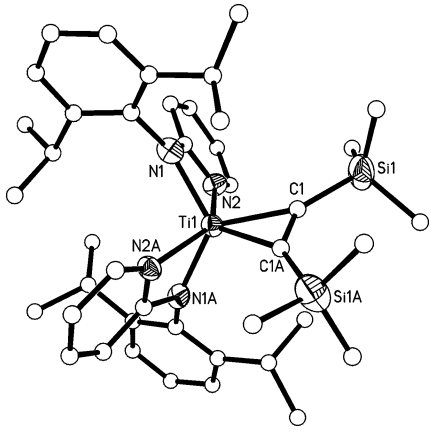


Figure 2. Molecular structure of **2** (ellipsoids correspond to the 50% probability level). Selected bond lengths (Å) and angles (°): C1–C1A 1.338(13), C1–Ti1 2.090(7), Ti1–N1 2.058(5), Ti1–N2 2.152(5); C1–C1A–Si1 138.9(2), C1–C1A–Ti1 71.33(18), N1–Ti1–N1A 121.4(3), C1–Ti1–C1A 37.3(4), N1–Ti1–N2 64.22(18).

In the solid state **2** is stable under argon at room temperature but rapidly decomposes in the presence of air and moisture.

It is noteworthy that in the ^1H NMR spectrum of **2** at room temperature there is a singlet corresponding to $SiMe_3$ at δ = 0.16 ppm, four doublets for the four diastereotropic methyl groups and two separate septets for CH protons of the aminopyridinato ligand at δ = 2.86 and 3.42 ppm. The ^{13}C NMR spectrum shows, in addition to other signals, the characteristic signal for carbon atoms of acetylene coordinated to Ti (δ = 209.7 ppm) which is comparatively upfield than what has been observed for other titanium-stabilized alkyne complexes indicating a weakly bound acetylene ligand.[2c,15] Reduction of **1** with KC_8 under N_2 atmosphere in the absence of any supporting ligand leads to a homoleptic tris(aminopyridinato)titanium complex **3**, the only product that could be isolated (Scheme 1) owing most probably due to ligand rearrangement. Since the paramagnetic nature of **3** prevents structural characterization by NMR spectroscopy, X-ray analysis was performed (Figure 3).[12] Only very weakly diffracting crystals of **3** could be obtained resulting in a low-quality structure, therefore detailed discussion of bond lengths and angles is waived. However, the connectivity was established.

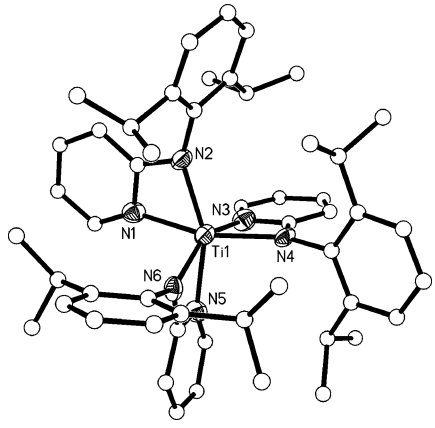


Figure 3. Molecular structure of **3** (ellipsoids correspond to the 50% probability level).

NMR-tube experiments indicate that **2** did not react with 1,4-bis(trimethylsilyl)-1,3-butadiyne even when harsh conditions were applied (a C_6D_6 sample of the mixture was heated at 110 °C for 48 hours). This experiment also indicates that **2** itself is rather stable in solution at high temperature since no decomposition was observed. Complex **2** is capable of insertion reactions as it reacts with one equivalent of acetone in hexane and gives **4** in quantitative yield. Complex **4** has been isolated as red crystals and X-ray analysis[12] reveals two independent molecules per asymmetric unit along with one hexane solvate molecule. The molecular structure of **4** is shown in Figure 4. The ^1H NMR spec-

trum of **4** shows two sets of signals for the non-equivalent $SiMe_3$ groups at δ = 0.26 and 0.42 ppm and two sets of signals for the aminopyridinato ligands. The C(1)–C(2) distance of 1.370(4) Å and the C3–O1 distance [1.432(3) Å] are in the expected ranges for C–X (X = C, O) bonds.[14]

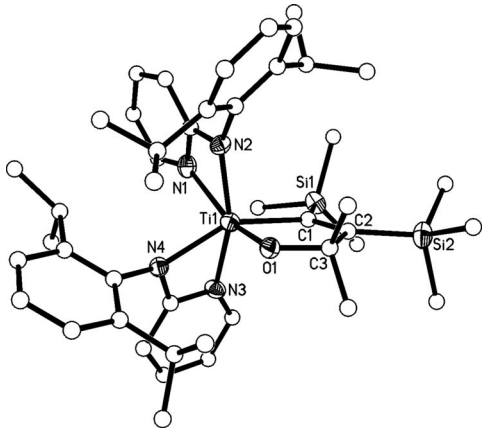


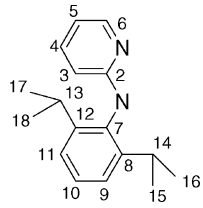
Figure 4. Molecular structure of **4** (ellipsoids correspond to the 50% probability level). Selected bond lengths (Å) and angles (°): C1–C2 1.370(4), C1–Ti1 2.178(3), C3–O1 1.432(3), Ti1–N1 2.263(3), Ti1–N2 2.008(3), O1–Ti1 1.776(2); O1–Ti1–C1 79.83(11), N2–Ti1–N1 61.99(10).

Conclusions

Complex **2** can be prepared from $[Ap_2TiCl_2]$ via reduction with magnesium in the presence of bis(trimethylsilyl)acetylene. The spectroscopic data of **2** justifies it having a weakly bound acetylene complex. Compound **2** is not only quite stable at room temperature but also at high temperature under argon atmosphere. The reduction of $[Ap_2TiCl_2]$ using KC_8 in the absence of any protecting ligand leads to a homoleptic tris(aminopyridinato)titanium complex. Complex **2** is capable of insertion reactions as it reacts with one equivalent of acetone. In future attempts we are interested in exploring the reactivity of **2** and related titanium as well as zirconium aminopyridinates.

Experimental Section

General Procedures: All manipulations were performed with rigorous exclusion of oxygen and moisture in Schlenk-type glassware on a dual manifold Schlenk line or in a N_2-filled glove box (mBraun 120-G) with a high-capacity recirculator (<0.1 ppm O_2). Solvents were dried by distillation from sodium wire/benzophenone. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were degassed, dried and distilled prior to use. NMR spectra were recorded with Bruker (250 MHz), Varian Inova (300 MHz) or Varian Inova (400 MHz) spectrometers at ambient temperature. Atom labelling is shown in Scheme 2. The chemical shifts are referenced to internal TMS for ^1H and ^{13}C.



Scheme 2. Atom numbering in Ap ligand of Ap complexes.

Synthesis of 1: Ether (15 mL) was added to 2-[(2,6-diisopropylphenyl)amino]pyridine (0.508 g, 2 mmol) and $(CH_3)_2NTiCl_3$ (0.198 g, 1 mmol) at ambient temperature. The resulting purple solution was stirred overnight and then filtered in order to separate a dark product. The filtrate was kept at low temperature to afford crystalline material; yield (0.598 g, 95.67%). $C_{34}H_{42}Cl_2N_4Ti{\cdot}C_7H_8$ (717.64): calcd. C 68.62, H 7.02, N 7.81; found C 68.50, H 7.12, N 7.68. ^1H NMR (250 MHz, C_6D_6): δ = 0.92 (d, J = 6.8 Hz, 12 H, $H^{15,16,17,18}$), 1.21 (d, J = 6.8 Hz, 12 H, $H^{15,16,17,18}$), 3.28 (br. s, 2 H, $H^{13,14}$), 5.52 (d, J = 8.4 Hz, 1 H, H^3), 5.96 (m, 2 H, H^5), 6.70 (m, 2 H, H^4), 7.10–7.18 (m, 6 H, $H^{9,10,11}$), 7.78 (d, J = 5.1 Hz, 2 H, H^6) ppm. ^{13}C NMR (63 MHz, C_6D_6): δ = 24.5 ($C^{15,16,17,18}$), 25.7 ($C^{15,16,17,18}$), 28.3 ($C^{13,14}$), 105.2 (C^3), 113.9 (C^5), 124.7 ($C^{9,11}$), 137.8 (C^4), 141.8 (C^4), 142.2 ($C^{8,12}$), 143.9 (C^7), 145.2 (C^6), 169.6 (C^2) ppm.

Synthesis of 2: Bis(trimethylsilyl)acetylene (0.44 mL, 1.92 mmol) was added to **1** (1.2 g, 1.92 mmol) and Mg (0.066 g, 2.72 mmol) in THF (20 mL). The solution was stirred overnight at room temperature during which time the colour changed from purple to blue. The solvent was evaporated in vacuo and the product extracted with hexane (2 × 20 mL). The filtrate was kept at low temperature to afford dark blue crystals of **2**; yield 0.632 g (45.4%). $C_{42}H_{60}N_4Si_2Ti$ (724.99): calcd. C 59.58, H 8.34, N 7.73; found C 58.97, H 8.21, N 7.76. ^1H NMR (300 MHz, C_6D_6): δ = 0.16 (s, 18 H, $SiMe_3$), 0.84 (d, J = 6.9 Hz, 6 H, $H^{15,16,17,18}$), 1.04 (d, J = 6.9 Hz, 6 H, $H^{15,16,17,18}$), 1.17 (d, J = 6.9 Hz, 6 H, $H^{15,16,/7,18}$), 1.20 (d, J = 6.9 Hz, 6 H, $H^{15,16,/7,18}$), 2.86 (sept, J = 6.9 Hz, 2 H, $H^{13,14}$), 3.42 (sept, J = 6.9 Hz, 2 H, $H^{13,14}$), 5.48 (d, J = 8.4 Hz, 2 H, H^3), 5.86 (t, J = 6.1 Hz, 2 H, H^5), 6.63 (t, J = 7.2 Hz, 2 H, H^4), 7.21 (m, 6 H, $H^{9,10,11}$), 7.68 (d, J = 5.1 Hz, 2 H, H^6) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 1.5 [$C_2(SiMe_3)_2$], 24.3 ($C^{15,16,17,18}$), 25.2 ($C^{15,16,17,18}$), 25.7 ($C^{15,16,17,18}$), 27.8 ($C^{13,14}$), 28.5 ($C^{13,14}$), 105.0 (C^3), 111.2 (C^5), 124.5 (d, $C^{9,11}$), 126.5 ($C^{9,11}$), 140.2 ($C^{8,12}$), 141.3 (C^{10}), 144.8 (C^4), 145.7 (C^7), 150.4 (C^6), 160.3 (C^2), 209.7 [$C_2(SiMe_3)_2$] ppm.

Synthesis of 3: THF (30 mL) was added to **1** (1.251 g, 2.00 mmol) and KC_8 (1.083 g, 8.00 mmol) at ambient temperature. Warming up was observed and suddenly the colour changed to black. The reaction mixture was stirred under N_2 for 24 hours. The solvent was evaporated in vacuo and the product extracted with hexane. The dark filtrate was kept at room temperature to afford red crystals of the product; yield 0.205 g (12.7%). $C_{51}H_{63}N_6Ti$ (807.95): calcd. C 75.81, H 7.86, N 10.40; found C 74.94, H 7.86, N 10.86. ^1H NMR (400 MHz, C_6D_6): δ = –11.79 (s), –8.33 (s), 0.38 (s), 0.86–1.23 (br. m), 1.40 (d), 1.62 (s), 2.98 (s), 3.57 (s), 4.05 (br. s), 5.78 (d), 6.11 (br. s), 6.94 (d), 7.02 (d), 7.96 (s), 8.38 (br. s), 9.82 (s) ppm.

Synthesis of 4: Acetone (0.02 mL, 0.28 mmol) was added to **2** (0.2 g, 0.28 mmol) in hexane (5 mL) at room temperature; the colour of the mixture changed from blue to dark red. The solution was stirred for five minutes and then kept at low temperature to

afford red crystals of **4**; yield 0.186 g (80.4%). $C_{45}H_{66}N_4OSi_2Ti$·0.5 hexane (826.16): calcd. C 69.78, H 8.91, N 6.78; found C 70.19, H 8.87, N 6.95. ^{1}H NMR (400 MHz, C_6D_6): δ = 0.26 (s, 9 H, -SiMe_3), 0.42 (s, 9 H, -SiMe_3), 0.72 (d, J = 6.6 Hz, 6 H, $H^{15,16,17,18}$), 0.87 (d, J = 6.6 Hz, 3 H, $H^{15,16,17,18}$), 1.12 (s, 3 H, CH_3), 1.18 (d, J = 6.6 Hz, 3 H, $H^{15,16,17,18}$), 1.20 (d, J = 6.6 Hz, 3 H, $H^{15,16,17,18}$), 1.28 (s, 3 H, H^{CH3}), 1.33 (d, J = 6.9 Hz, 3 H, $H^{15/16/17/18}$), 1.50 (d, J = 6.9 Hz, 3 H, $H^{15/16/17/18}$), 2.22 (sept, J = 6.6 Hz, 1 H, $H^{13/14}$), 2.35 (sept, J = 6.6 Hz, 1 H, $H^{13/14}$), 3.87 (sept, J = 6.9 Hz, 1 H, $H^{13/14}$), 4.06 (sept, J = 6.9 Hz, 1 H, $H^{13/14}$), 5.60 (d, J = 8.5 Hz, 1 H, H^3), 5.73 (d, J = 8.7 Hz, 1 H, H^3), 5.90 (t, J = 6.4 Hz, 1 H, H^5), 6.06 (t, J = 6.0 Hz, 1 H, H^5), 6.72 (m, 1 H, H^4), 6.87 (m, 1 H, H^4), 7.04–7.31 (m, 6 H, $H^{9,10,11}$), 7.69 (dd, 1 H, H^6), 8.20 (dd, 1 H, H^6) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 4.5 (-$SiMe_3$), 6.0 (-$SiMe_3$), 25.0 ($C^{15,16,17,18}$), 25.2 ($C^{15,16,17,18}$), 25.7 ($C^{15,16,17,18}$), 26.3 ($C^{15,16,17,18}$), 27.3 ($C^{15,16/17,18}$), 27.6 ($C^{15,16/17,18}$), 28.2 ($C^{13/14}$), 28.4 ($C^{13/14}$), 28.6 ($C^{13/14}$), 28.7 ($C^{13/14}$), 29.2 (C^{CH3}), 31.9 (C^{CH3}), 92.8 (CO), 106.0 (C^3), 107.3 (C^3), 108.7 (C^5), 111.4 (C^5), 123.2 ($C^{9/11}$), 124.0 ($C^{9/11}$), 124.6 ($C^{9/11}$), 125.4 ($C^{9/11}$), 125.7 ($C^{9/11}$), 126.6 ($C^{9/11}$), 139.9 ($C^{8,12}$), 140.8 ($C^{8,12}$), 143.7 (C^4), 143.9 (C^4), 144.6 (C^{10}), 144.7 (C^7), 145.1 (C^7), 145.4 (C^6), 145.7 (C^6), 170.2 (C^2), 173.0 (Ti-C=C*), 186.9 (Ti-C*=C) ppm.

Acknowledgments

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[1] U. Rosenthal, V. V. Burlakov, *Organometallic Chemistry of Titanocene and Zirconocene Complexes with Bis(trimethylsilyl) acetylene as the Basis for Applications in Organic Synthesis*, in: *Titanium and Zirconium in Organic Synthesis* (Ed.: I. Marek), Wiley-VCH, New York, **2002**, pp. 355–389.

[2] a) A. Ohff, S. Pulst, C. Lefeber, N. Peulecke, P. Arndt, V. V. Burlakov, U. Rosenthal, *Synlett* **1996**, 111–118; b) U. Rosenthal, P.-M. Pellny, F. G. Kirchbauer, V. V. Burlakov, *Acc. Chem. Res.* **2000**, *33*, 119–129; c) U. Rosenthal, V. V. Burlakov, P. Arndt, W. Baumann, A. Spannenberg, *Organometallics* **2003**, *22*, 884–900; d) U. Rosenthal, P. Arndt, W. Baumann, V. V. Burlakov, A. Spannenberg, *J. Organomet. Chem.* **2003**, *670*, 84–96; e) U. Rosenthal, *Angew. Chem.* **2003**, *115*, 1838–1842; *Angew. Chem. Int. Ed.* **2003**, *42*, 1794–1798; f) A. Spannenberg, P. Arndt, W. Baumann, U. Rosenthal, *J. Organomet. Chem.* **2003**, *683*, 261–266; g) U. Rosenthal, *Angew. Chem.* **2004**, *116*, 3972–3977; *Angew. Chem. Int. Ed.* **2004**, *43*, 3882–3887; h) U. Rosenthal, V. V. Burlakov, P. Arndt, W. Baumann, A. Spannenberg, V. B. Shur, *Eur. J. Inorg. Chem.* **2004**, 4739–4749; i) U. Rosenthal, V. V. Burlakov, P. Arndt, W. Baumann, A. Spannenberg, *Organometallics* **2005**; *24*, 456–471; j) U. Rosenthal, in *Acetylene Chemistry II. Chemistry, Biology, and Material Science* (Eds.: F. Diederich, P. J. Stang, R. R. Tykwinski), Wiley-VCH, Weinheim, **2003**, chapter 4, p. 139–171.

[3] a) L. K. Woo, J. A. Hays, R. A. Jacobson, C. L. Day, *Organometallics* **1991**, *10*, 2102–2104; b) Y. Gao, K. Harada, F. Sato, *Tetrahedron Lett.* **1997**, *36*, 5913–5916; c) E. S. Johnson, G. J. Balaich, P. E. Fanwick, I. P. Rothwell, *J. Am. Chem. Soc.* **1997**, *119*, 11086–11087; d) P. N. Riley, P. E. Fanwick, I. P. Rothwell, *Chem. Commun.* **1997**, 1109–1110; e) M. Horacek, J. Hiller, U. Thewalt, P. Stepnicka, K. Mach, *J. Organomet. Chem.* **1998**, *571*, 77–82; f) Jinyuan Chen, I. A. Guzei, L. K. Woo, *Inorg. Chem.* **2000**, *39*, 3715–3717; g) P. N. Riley, P. E. Fanwick, I. P. Rothwell, *J. Chem. Soc., Dalton Trans.* **2001**, 181–186; h) B. C. Bailey, Hongjun Fan, J. C. Huffman, Mu-Hyun Baik, D. J. Mindiola, *J. Am. Chem. Soc.* **2006**, *128*, 6798–6799; i) G. B. Nikiforov, P. Credson, S. Gambarotta, I. Korobkov, P. H. M. Budzelaar, *Organometallics* **2007**, *26*, 48–55.

[4] For review articles on aminopyridinato ligands see: a) R. Kempe, *Angew. Chem.* **2000**, *112*, 478–504; *Angew. Chem. Int. Ed.* **2000**, *39*, 468–493; b) R. Kempe, H. Noss, T. Irrgang, *J. Organomet. Chem.* **2002**, *647*, 12–20; c) R. Kempe, *Eur. J. Inorg. Chem.* **2003**, 791–803.

[5] a) N. M. Scott, T. Schareina, O. Tok, R. Kempe, *Eur. J. Inorg. Chem.* **2004**, 3297–3304; b) N. M. Scott, R. Kempe, *Eur. J. Inorg. Chem.* **2005**, 1319–1324; c) W. P. Kretschmer, A. Meetsma, B. Hessen, T. Schmalz, S. Qayyum, R. Kempe, *Chem. Eur. J.* **2006**, *12*, 8969–8978; d) W. P. Kretschmer, A. Meetsma, B. Hessen, N. M. Scott, S. Qayyum, R. Kempe, *Z. Anorg. Allg. Chem.* **2006**, *632*, 1936–1938; e) W. P. Kretschmer, B. Hessen, A. Noor, N. M. Scott, R. Kempe, *J. Organomet. Chem.* **2007**, *692*, 4569–4579; f) S. M. Guillaume, M. Schappacher, N. M. Scott, R. Kempe, *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 3611–3619; g) A. M. Dietel, O. Tok, R. Kempe, *Eur. J. Inorg. Chem.* **2007**, 4583–4586; h) R. Kempe, *Chem. Eur. J.* **2007**, *13*, 2764–2773; i) G. G. Skvortsov, G. K. Fukin, A. A. Trifonov, A. Noor, C. Doring, R. Kempe, *Organometallics* **2007**, *26*, 5770–5773; j) S. Qayyum, K. Haberland, C. M. Forsyth, P. C. Junk, G. B. Deacon, R. Kempe, *Eur. J. Inorg. Chem.* **2008**, 557–562.

[6] a) M. Polamo, M. Talja, A. J. Piironen, *Z. Kristallogr. NCS* **2005**, *220*, 41–42; b) A. Noor, W. Kretschmer, R. Kempe, *Eur. J. Inorg. Chem.* **2006**, 2683–2689.

[7] E. Benzing, W. Kornicker, *Chem. Ber.* **1961**, *94*, 2263–2267.

[8] M. Talja, M. Klinga, M. Polamo, E. Aitola, M. Leskelä, *Inorg. Chim. Acta* **2005**, *358*, 1061–1067.

[9] M. Talja, T. Luhtanen, M. Polamo, M. Klinga, T. A. Pakkanen, M. Leskelä, *Inorganica Chimica Acta* in press. doi: 10.1016/j.ica.2007.11.028.

[10] V. B. Shur, S. Z. Bernadyuk, V. V. Burlakov, M. E. Vol'pin, *IInd All-Union Conf. Organomet. Chem. Abs.*, Gorky, **1982**, 178.

[11] V. B. Shur, V. V. Burlakov, M. E. Vol'pin, *J. Organomet. Chem.* **1988**, *347*, 77–83.

[12] Selected details of the X-ray crystal structure analyses for **1**·2C_7H_8: space group: $P2(1)2(1)2(1)$, a = 32.213(3) Å, b = 9.2810(10) Å, c = 14.6820(18) Å; V = 4389.5(8) Å^3, z = 4, reflections collected/unique/observed: 38832/7336/3110, parameters: 498, R (obs.) = 0.0787, wR^2 (all data) = 0.1991, wR^2 (obs.) = 0.1711; **2**: space group: $P3(2)21$, a = 19.4919(14) Å, b = 19.4919(15) Å, c = 9.4918(7) Å; V = 3123.1(4) Å^3, z = 3, reflections collected/unique/observed: 29109/2736/2231, parameters: 229, R (obs.) = 0.0741, wR^2 (all data) = 0.1522, wR^2 (obs.) = 0.1444; **3**: space group: $P2(1)/c$, a = 13.3860 (11) Å, b = 13.3220 (11) Å, c = 25.739 (2) Å; β = 99.441(7) °, V = 4527.8 (7) Å^3, z = 4, reflections collected/unique/observed: 8598/8598/3463, parameters: 523, R (obs.) = 0.1059, wR^2 (all data) = 0.2251, wR^2 (obs.) = 0.1781; **4**: space group: $P\bar{1}$, a = 10.4280(8) Å, b = 13.532(11) Å, c = 18.1300(15) Å; α = 95.933(6), β = 106.305(6), γ = 101.491(6) °, V = 2371.5(3) Å^3, z = 2, reflections collected/unique/observed: 8950/8950/3513, parameters: 511, R (obs.) = 0.0425, wR^2 (all data) = 0.0805, wR^2 (obs.) = 0.0692; X-ray crystal structure analysis was carried out with a STOE IPDS II diffractometer equipped with an Oxford Cryostream low-temperature unit. CCDC-676560 (for **1**), -676561 (for **2**), -676562 (for **3**) and -676563 (for **4**) contain the supplementary crystallographic data for 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.

[13] S. Deeken, G. Motz, R. Kempe, *Z. Anorg. Allg. Chem.* **2007**, *633*, 320–325.

[14] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

[15] a) V. V. Burlakov, A. V. Polyakov, A. I. Yanovsky, Yu. T. Struchkov, V. B. Shur, M. E. Vol′pin, *J. Organomet. Chem.* **1994**, *476*, 197–206; b) G. Schmid, U. Thewalt, M. Polasek, K.

Mach, P. Sedmera, *J. Organomet. Chem.* **1994**, *482*, 231–241; c) V. Varga, K. Mach, M. Polasek, P. Sedmera, J. Hiller, U. Thewalt, S. I. Troyanov, *J. Organomet. Chem.* **1996**, *506*, 241–251; d) V. Varga, J. Hiller, R. Gyepes, M. Polasek, P. Sedmerad, U. Thewalt, K. Mach, *J. Organomet. Chem.* **1997**, *538*, 63–74; e) M. Horaćek, V. Kupfer, U. Thewalt, P. Stepnicka, M. Polasek, K. Mach, *Organometallics* **1999**, *18*, 3572–3578; f) M. Horacek, P. Stepnicka, S. Gentil, K. Fejfarova, J. Kubista, N. Pirio, P. Meunier, F. Gallou, L. A. Paquette, K. Mach, *J. Organomet. Chem.* **2002**, *656*, 81–88; g) M. Horacek, P. Stepnika, J. Kubista, R. Gyepes, I. Cisarova, L. Petrusova, K. Mach, *J. Organomet. Chem.* **2002**, *658*, 235–241; h) M. Horacek, P. Stepnicka, J. Kubista, I. Cisarova, L. Petrusova, K. Mach, *J. Organomet. Chem.* **2003**, *667*, 154–166.

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