chromatography on a silica gel column with MeOH/ethyl acetate (5/95) as eluent to give **6** (3.4 g, 32% yield).

1: Compound **6** (3.0 g, 1.9 mmol) was treated with methanolic ammonia (50 mL) and stirred at room temperature overnight. After chromatographic purification on silica gel with hexane/ethyl acetate (4/1) as eluent, **1** was obtained as a fluorescent yellow solid (2.3 g, 80% yield). ^{1}H NMR (500 MHz, C_6H_6): $\delta = 13.63$ (s, 2H, NH), 11.22 (d, $J = 14.2$ Hz, 2H, NH_2), 9.83 (s, 1H, H9), 9.12 (dd, $J = 5.3$, 14.2 Hz, 2H, N=CH), 8.12 (s, 1H, H10), 7.71 (d, $J = 8.9$ Hz, 2H, H4, H5), 7.53 (d, $J = 6.89$ Hz, 2H, H2, H7), 7.06 (dd, $J = 8.7$, 6.7 Hz, 2H, H3, H6), 6.67 (d, $J = 8.15$ Hz, 2H, H1′), 5.33–5.31 (m, 4H, H2′, H5′), 5.29 (br s, 2H, NH_2), 4.47–4.44 (m, 4H, H3′, H4′), 3.98–3.88 (m, 2H, H5′), 1.67–0.53 (ss, 90H, 6Si$(CH_3)_2C(CH_3)_3$); ^{13}C NMR (125 MHz, C_6H_6): $\delta = 160.3$ (C6′), 160.1 (N=CH), 156.5 (C2′), 150.7 (C4′), 136.1, 133.1, 132.0 (aromatic C), 131.6 (C2), 129.9 (C4), 128.3 (C10), 125.2 (C3), 124.1 (C9), 122.0 (C8′), 120.1 (C5′), 92.5 (alkynyl C), 87.9 (C1″), 85.9 (alkynyl C), 85.7 (C4″), 74.4 (C3″), 71.8 (C2"), 64.5 (C5″), 26.6, 25.9, 25.0 ($SiMe_2C(CH_3)_3$), 18.6, 18.1, 17.5 ($SiMe_2CMe_3$), −4.4, −4.6, −4.7, −4.8, −5.3 ($Si(CH_3)_2CMe_3$); FAB-MS: m/z 1527 [M^+]; high-resolution FAB-MS calcd for $C_{76}H_{119}N_{12}O_{10}Si_6$: 1527.7788 [$M^+$ of **1**], found: 1527.7752; FAB-MS 3054; high-resolution FAB-MS calcd for $C_{152}H_{238}N_{24}O_{20}Si_{12}$: 3054.550 ($M^+$ of the dimer), found: 3054.549; elemental analysis calcd for $C_{76}H_{119}N_{12}O_{10}Si_6$: C 59.73, H 7.79, N 11.01; found C 59.74, H 7.69, N 10.86.

2: Compound **1** (0.3 g, 0.2 mmol) was treated with ammonia saturated in methanol/$CHCl_3$ (1/1, 20 mL) at 100°C in a sealed tube overnight. The solvents were removed under reduced pressure with a rotary evaporator, and the residue was subjected to chromatography on a silica gel column with MeOH/$CHCl_3$ (7/93) as eluent to give **2** (0.15 g, 52% yield). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 12.65$ (s, 2H), 9.33 (s, 1H), 8.57 (s, 1H), 8.14 (d, $J = 8.7$ Hz, 2H), 7.92 (d, $J = 6.6$ Hz, 2H), 7.54 (t, $J = 8.1$ Hz, 2H), 6.13 (d, $J = 5.1$ Hz, 2H), 5.50 (br, 4H), 5.19 (m, 2H), 4.13 (d, $J = 3.9$ Hz, 2H), 3.83 (m, 6H), 0.96–0.63 (m, 90H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 159.1$, 153.4, 151.8, 133.1, 131.9, 131.5, 131.2, 130.8, 128.3, 125.4, 124.0, 119.0, 116.8, 93.4, 88.8, 86.4, 82.6, 73.3, 71.0, 62.7, 25.9, 25.6, 24.9, 18.01, 17.8, 17.7, −4.6, −4.7, −4.9, −5.9, −6.0, −6.4; CI-MS: m/z 1472 [M^+]; high-resolution CI-MS calcd for $C_{74}H_{116}N_{10}O_{10}Si_6$: 1472.7492 [$M^+$] of **2**; found: 1472.7477.

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[10] A weak signal ascribable to a dimeric species was observed in the mass spectrum of **2**. However, the signal in question was not sufficiently intense to allow for a high-resolution analysis.

[11] The assignment of the resonances in the ^{1}H NMR spectrum of **1** is based on information gleaned from the COSY and HMQC NMR spectroscopic analyses (^{1}H–^{13}C and ^{1}H–^{15}N).

[12] Similar shifts were also observed in C_6D_6 and [D$_8$]toluene. Unfortunately, **2**, **6**, and **7** are insoluble in these solvents. Thus, initial comparative analyses were carried out in $CDCl_3$.

[13] The broad ^{1}H NMR signal for the amino groups of **2** in $CDCl_3$ is due to fast exchange between the two free NH_2 protons. Further support for this conclusion came from the observation that sharp signals, ascribable to the amino groups in question, were seen in the ^{1}H NMR spectra of both **7** in $CDCl_3$ (where no proton is available for exchange) and **2** in [D$_6$]DMSO (where both NH_2 protons are hydrogen-bonded to [D$_6$]DMSO).

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[15] Several features of 2D ROESY spectrum of **1** in C_6D_6 are noteworthy. First, the intense cross peaks observed between H1″ at $\delta = 6.7$ and H9 at $\delta = 9.8$ as well as between N=CH at $\delta = 9.1$ and H5″ at $\delta = 5.3$ and 3.9 provide evidence for the *syn* conformation of the glycoside bond. Secondly, the observation of intense cross peaks between the imino NH proton at $\delta = 13.6$ and the hydrogen-bonded proton of NH_2 at $\delta = 11.2$, coupled with presence of a much weaker cross peak involving this imino NH proton and the N=CH proton and no cross peak with the non-hydrogen-bonded proton of NH_2 at $\delta = 5.2$, provide evidence for the *cis* configuration of the N=CH bond. Finally, the intense cross peak observed between the signals at $\delta = 13.6$ for the imino NH proton and at $\delta = 11.2$ for the hydrogen-bonded NH_2 proton provides evidence of close proximity of these two protons.

[16] a) The *syn* conformation is also believed to play a critical role during the synthesis because only it allows the 8-position to be most susceptible to nucleophilic attack by its coupling partner; b) both a *syn* conformation of the glycosidic bond and a *cis* configuration of the C=N bond are assigned to **6** on the basis of NMR spectral similarities.

[17] The fact that the lone pairs of the two carbonyl oxygen atoms are tied up in hydrogen bonding is believed to contribute to the nonpolarity of **1**.

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[19] The insolubility of **1** under the conditions of the experiment precluded the use of the more strongly hydrogen bonding solvent water.

[20] The coalescence observed at higher temperature is the result of fast exchanges between different states of DMSO-derived solvation of the four amino protons. This gives rise to an average chemical shift for these protons; at lower temperature, however, the relevant exchange processes are slow enough on the NMR time scale that multiple resonances are observed.

Tethered Bis-Amidinates as Supporting Ligands: A Concerted Elimination/$\sigma - \pi$ Rearrangement Reaction Forming an Unusual Titanium Arene Complex**

John R. Hagadorn and John Arnold*

Development of ligands that play supporting roles in organotransition metal chemistry has been the subject of intense interest for many years. We are exploring amidinates in this regard as they display attractive properties from a synthetic standpoint. Well characterized titanium derivatives, that utilized the *N,N′*-bis(trimethylsilyl)benzamidinate li-

[*] Prof. J. Arnold, J. R. Hagadorn
Department of Chemistry, University of California
Berkeley, CA 94720–1460 (USA)
E-mail: arnold@socrates.berkeley.edu

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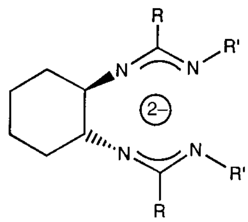
gand[1–3] were first reported in 1988 by Dehnicke et al.[4] and Roesky et al.[5] Numerous workers have since begun exploring the reaction chemistry of this class of compounds.[6–8] We were interested in examining more robust nonsilylated amidinate ligands[9] in which two amidinate functionalities were linked together in a constrained manner analogous to ansa-cyclopentadienyls. Additionally, we sought to introduce chirality to explore the potential of transition metal amidinates in enantioselective transformations. Our initial focus is on cyclohexane-linked amidinates. Here we describe the preparation of racemic titanium derivatives and an η^6-toluene complex with an unusual puckered C_6 ring[10] which labeling studies suggest is formed by an intramolecular $\sigma-\pi$ rearrangement of a putative benzyl hydride complex as intermediate – a mechanism which we believe to be unprecedented in the formation of transition metal arene complexes.[11]



L^x, X = H : R = Ph, R' = Ph
X = Me : R = 4-MeC_6H_4, R' = Ph

Cyclohexane-linked amidinate ligands L^x were isolated in moderate yields (ca. 40%) from the reaction of the cyclohexane-linked diamides with PCl_5 and substituted aniline compounds.[12] The reaction of $(L^x)H_2$ with $[Ti(CH_2Ph)_4]$ in toluene produced the dibenzyl derivatives $[(L^x)Ti(CH_2Ph)_2]$, which were isolated in high yields as red crystals from Et_2O [Eq. (1)].

$$(L^x)H_2 + [Ti(CH_2Ph)_4] \longrightarrow [(L^x)Ti(CH_2Ph)_2] + 2\,PhCH_3 \qquad (1)$$

The dibenzyl complex $[(L^{Me})Ti(CH_2Ph)_2]$ reacts with H_2 (25 psig, (1.7 bar)) overnight in C_6D_6 with liberation of one equivalent of $PhCH_3$ to form a compound with a complex NMR spectrum that lacked the twofold axis of symmetry of the starting material. A preparative scale reaction carried out in toluene gave a solution which upon removal of the volatile materials afforded an oily solid. Crystallization from Et_2O afforded the product as dark red prisms in good yield. IR spectroscopy failed to reveal any signals that could be attributed to a $\nu_{Ti\text{-}H}$ absorption, and the compound failed to react with two equivalents of $CHCl_3$ in C_6D_6 solution over 2 h. X-Ray crystallography[13] (Figure 1) revealed the product to be the η^6-toluene complex $[(L^{Me})Ti(\eta^6\text{-}PhCH_3)]$. To accommodate the η^6-arene, the titanium atom is forced out of the N_4 plane to form a pseudo piano-stool structure. Metrical parameters (Figure 2) suggest a significant contribution from a highly reduced cyclohexadiene dianion resonance structure resulting in the diamagnetic complex having substantial Ti^{IV} character. Accordingly, the arene ligand is puckered:[14] the two planes defined as C4-C5-C6-C7 and C7-C2-C3-C4 intersect with a dihedral angle of 20.0°, which implies appreciable sp^3 character at C4 and C7. The Ti-C bonds also reflect this trend with much shorter Ti–C4 (2.202(4) Å) and Ti–C7 (2.233(4) Å) bonds than the other four Ti–C interactions (2.35-2.42 Å). This is in contrast to the situation previously reported $Ti^{II}\eta^6$-arene complexes (generally prepared by Friedel–Crafts reductive synthesis in the presence of an arene), which show longer, roughly equivalent Ti–C bonds (ca. 2.50 Å).[15–21] Likewise, the C–C bonds in $[(L^{Me})Ti(\eta^6\text{-}PhCH_3)]$ are atypical with short C2–C3 and C5–C6 interactions of 1.371(5) and 1.358(6) Å, respectively, and longer C2–C7, C3–C4, C4–C5, and C6–C7 bonds of 1.444(5), 1.429(5), 1.429(5), and 1.433(5) Å, respectively, again suggestive of cyclohexadiene-like character.

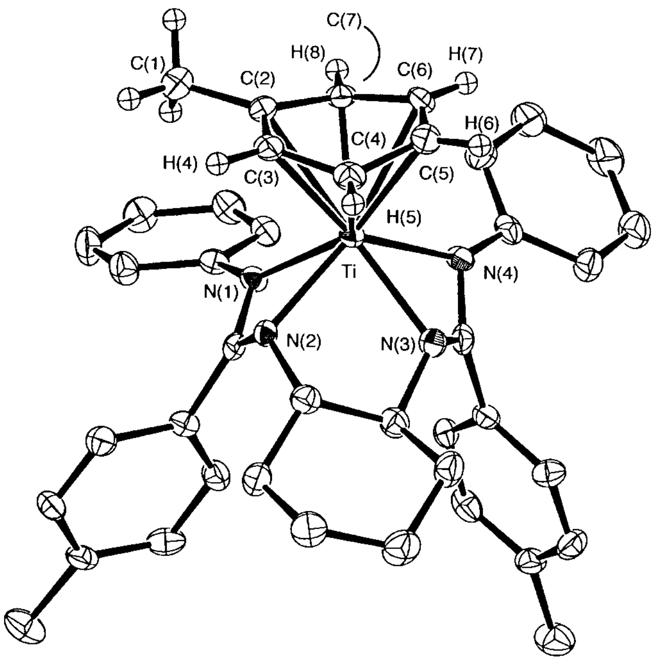


Figure 1. ORTEP view of $[(L^{Me})Ti(\eta^6\text{-}PhCH_3)]$ drawn with 50% thermal ellipsoids.

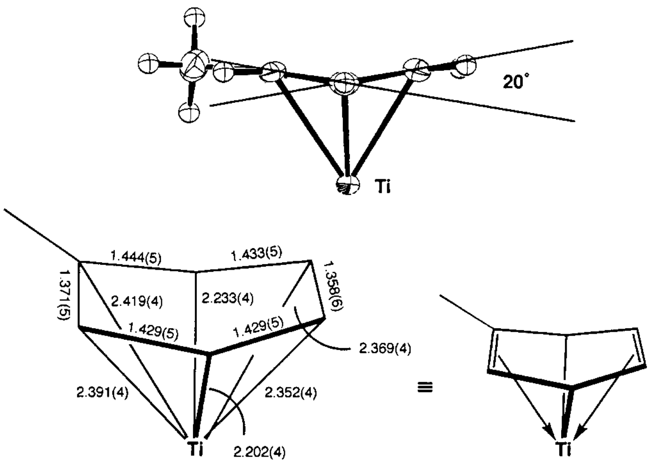


Figure 2. Metrical parameters of the η^6-toluene ligand of $[(L^{Me})Ti(\eta^6\text{-}PhCH_3)]$. All distances are given in Å.

Our data suggest that the reaction proceeds as shown in Scheme 1 via a transient Ti–H species that is too short-lived to detect directly. Evidence for this pathway includes the following: 1) Exclusive formation of $[(L^{Me})Ti(\eta^6\text{-}PhCDH_2)]$ when the dibenzyl complex was treated with D_2 (80 psig, 5.5 bar) in toluene. 2) Liberation of free $PhCH_3$ and $PhCDH_2$ in a 2.1:1 ratio and the formation of the titanium arene species $[(L^{Me})Ti(\eta^6\text{-}PhCH_3)]$ and $[(L^{Me})Ti(\eta^6\text{-}PhCDH_2)]$ in a ratio of 1.5:1.on carrying out the reaction using a 1:1 mixture of H_2 and D_2. In addition, ^1H NMR spectroscopy showed the formation of substantial quantities of HD. 3) Further evidence of the

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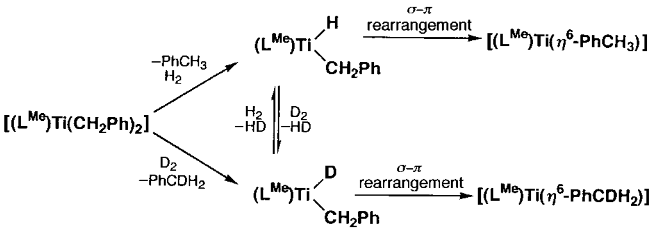

Scheme 1. Reaction pathway of the elimination and σ–π rearrangement.

involvement of a transient hydride is the observation of rapid olefin hydrogenation when an excess of ethylene was added to a solution of the dibenzyl complex in the presence of hydrogen.

These data may be rationalized by a mechanism that involves initial formation of toluene and a reactive benzyl hydride complex that undergoes further hydrogenolysis leading to scrambling of H_2 and D_2 to HD.[22] Elimination of the benzyl and hydride ligands (by C–H coupling) and σ–π rearrangement leads to the isolated (η^6-arene) complex.

In summary, the use of the bis-amidinates with constrained geometry has led to some highly unusual chemistry not seen in previously reported transition metal amidinate complexes or in related metallocene systems. Further studies of these and enantiomerically pure linked-amidinates are in progress.

Experimental Section

$[(L^{Me})Ti(CH_2Ph)_2]\cdot 0.5\,Et_2O$: A suspension of $(L^{Me})H_2$ (4.61 g, 9.21 mmol) in toluene (25 mL) was added to a solution (20 mL) of $[Ti(CH_2Ph)_4]$ (3.80 g, 9,21 mmol) in toluene at −20 °C. The mixture was allowed to warm to room temperature. After 5 h the volatiles were removed under reduced pressure to give a red oil. The compound was crystallized from toluene/Et_2O (5.15 g, 73%); m.p. 169–170 °C; ^{1}H NMR (C_6D_6): δ = 7.41 (d, J = 7.5 Hz, 4H), 7.15 (m, 12H), 7.02 (d, J = 8.0 Hz, 4H), 6.87 (m, 8H), 3.70 (d, J = 8.6 Hz, 2H), 3.57 (d, J = 8.6 Hz, 2H), 3.24 (q, J = 7 Hz, 2H), 3.12 (m, 2H), 1.94 (s, 6H), 1.40 (m, 2H), 1.09 (t, J = 7 Hz, 3H), 1.08 (m, 4H), 0.75 (m, 2H); $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 171.3, 147.6, 146.7, 139.9, 130.6, 129.6, 129.1, 128.6, 123.4, 122.9, 122.1, 91.1, 68.9, 65.9, 33.9, 24.8, 21.3, 15.6; IR (mineral oil): $\tilde{\nu}$ = 1594 (m), 1530 (m), 1462 (vs, br), 1340 (m), 1312 (m), 1267 (m), 1236 (w), 1207 (w), 1181 (w), 1141 (w), 1080 (w), 1020 (w), 960 (m), 828 (m), 765 (w), 741 (m), 693 (m), 510 (w), 483 (w) cm^{-1}; elemental analysis calcd for $[LTi(CH_2Ph)_2]$ ($C_{46}H_{44}N_4Ti$): C 78.84; H 6.33; N 7.99; found: C 78.59; H 6.05; N 7.87.

$[(L^{Me})Ti(\eta^6\text{-toluene})]\cdot 0.5\,Et_2O$: Toluene (20 mL) was added to (L^{Me})-$Ti(CH_2Ph)_2\cdot 0.5(Et_2O)$ (2.00 g, 2.61 mmol) in a Fischer–Porter bottle, and the bottle was pressurized with H_2 (80 psig, 5.5 bar). After stirring overnight the volatiles were removed under reduced pressure affording a dark red oil. The compound was crystallized from Et_2O at −30 °C (1.27 g, 72%). M.p.: 170 °C (decomp); ^{1}H NMR (C_6D_6): δ = 8.01 (br, 2H), 7.59 (br, 1H), 7.36 (br, 1H), 7.05–6.91 (m, 8H), 6.82 (br, 1H), 6.77–6.64 (m, 5H), 4.68 (t, J = 7.6 Hz, 1H), 4.50 (m, 2H), 4.32 (d, J = 6.4 Hz, 1H), 4.23 (d, J = 6.5 Hz, 1H), 3.91 (m, 1H), 3.72 (m, 1H), 3.26 (q, J = 7.0 Hz, 2H), 2.30 (m, 1H), 2.01 (s, 3H), 1.90 (m, 1H), 1.86 (s, 3H), 1.60 (m, 1H), 1.48 (m, 1H), 1.39 (m, 1H), 1.11 (t, J = 7.0 Hz, 3H), 1.06 (m, 1H), 0.99 (s, 3H), 0.87 (m, 2H); $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 168.0, 159.5, 150.3, 149.3, 140.0, 139.0, 133.7, 131.9, 131.5, 131.2, 129.7, 128.5, 124.0, 122.8, 121.7, 121.7, 120.1, 110.4, 109.4, 108.7, 108.2, 75.3, 71.6, 65.9, 37.6, 35.0, 27.1, 25.5, 21.4, 21.3, 21.1, 15.5; IR (mineral oil): $\tilde{\nu}$ = 1594 (m), 1568 (w), 1496 (m), 1463 (vs, br), 1265 (m), 1211(w), 1181(w), 1150 (w), 1110 (w), 1081 (w), 1059 (w), 1020 (w), 954 (w), 830 (m), 742 (m), 723 (w), 692 (m), 631 (w), 525 (w), 508 (w), 473 (w) cm^{-1}; elemental analysis calcd for $C_{43}H_{47}N_4O_{0.5}Ti$: C 76.12; H 7.00; N 8.45; found: C 75.85; H 7.05; N 8.26.

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[13] $[(L^{Me})Ti(\eta^6\text{-}PhCH_3)]\cdot 0.5\ Et_2O$: crystal dimensions $0.17\times0.12\times0.07$ mm, monoclinic, $C2/c$, a = 27.4848(6), b = 11.8724(3), c = 22.9332(3) Å, β = 105.504(1)°, V = 7211.0(4) Å^3, Z = 8, ρ_{calcd} = 1.245 g cm^{-3}, T = −130 °C, μ = 0.275 mm^{-1}, T_{min} = 0.876, T_{max} = 0.996, no. of reflections = 14725 (5380 unique), no. of observations = 3167, no. of parameters = 470, R = 0.0381, R_w = 0.0436, GOF = 1.346. Data were collected on a Siemens SMART CCD area detector ($Mo_{K\alpha}$ radiation, $0 < 2\theta < 46.5°$, 0.3° ω scans) and integrated with SAINT (4.024 ed, Siemens Industrial Automation, Inc.). The data were corrected for Lorentz and polarization effects, and a semiempirical absorption correction was applied with SADABS (Siemens). The structure was solved and refined (against $|F^2|$) with the TEXSAN (Molecular Structure Corporation, 1992) software package using direct methods. All non-H atoms were refined anisotropically. The hydrogens of the η^6-toluene ligand were located in a difference Fourier map and were refined isotropically. Remaining hydrogens were assigned idealized positions and were not refined. Residual electron-density extremes were 0.315 and −0.296 e Å^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100894. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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