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Reduction of Titanium Supported by a σ-/π-Bonded Tripyrrole Ligand: Ligand C−N Bond Cleavage and Coordination of Olefin and Arene with an Inverse Sandwich Structure

Grigory B. Nikiforov, Patrick Crewdson, Sandro Gambarotta,* Ilia Korobkov, and Peter H. M. Budzelaar*

Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada, and Department of Chemistry, University of Manitoba, R3T 2N2, Winnipeg, Manitoba, Canada

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The formally Ti(I)/Ti(II) mixed-valence toluene complex $\{2,5\text{-}[(C_4H_3N)CPh_2]_2[C_4H_2N(Me)]\}Ti$ (μ,η^6-C_7H_8)$Ti[\{2,5\text{-}[(C_4H_3N)CPh_2]_2[C_4H_2N(Me)]\}][K(DME)_2]\cdot$toluene (**1**) with an inverse sandwich type of structure has been obtained from the reduction of $\{2,5\text{-}[(C_4H_3N)CPh_2]_2[C_4H_2N(Me)]\}TiCl$ with potassium in toluene. The bridging molecule of toluene in the paramagnetic **1** shows a visible distortion due to a substantial amount of metal-to-ring back-bonding. Complex **1** was always the only detectable product, even in cases when lower than stoichiometric amounts of reductant were employed. DFT calculations have been carried out to elucidate the electronic structure of the mixed-valence **1** in order to clarify the reason for its apparent thermodynamic stability. The most energetically favorable model comprises two divalent Ti centers connected to an organic radical anion. The olefin adducts $\{2,5\text{-}[(C_4H_3N)CPh_2]_2$-$[C_4H_2N]\}Ti(\eta^2$-*trans*-PhHC═CHPh)[K(DME)] (**2**) and $\{2,5\text{-}[(C_4H_3N)CPh_2]_2[C_4H_2N\ (Me)]\}Ti(\eta^2$-*trans*-PhHC═CHPh) (**3**) were obtained from identical reactions carried out in the presence of *trans*-stilbene. Complexes **2** and **3** may be regarded as the result of the oxidative addition of a transient divalent species to the *trans*-stilbene molecule. In the case of **2** however, the reaction is accompanied by the cleavage of the C−N bond of the π-bound alkylated pyrrole ring.

Introduction

Extreme reactivity is the defining characteristic of divalent titanium chemistry as emphasized by the ability of these complexes to bind dinitrogen with a variety of bonding modes.[1] The strong reducing power of divalent titanium is commonly used to afford reductive transformation of organic substrates,[2] and in situ generated Ti(II) species have been widely used for a remarkable variety of metal-promoted organic transformations ranging from the McMurry reaction[3] and pinacol coupling[4] to enantioselective radical reactions.[5] Divalent titanium complexes are also particularly versatile in C−C bond forming reactions, such as the reductive coupling of olefins and acetylenes[6] and in some case were even claimed to be active polymerization catalysts.[7]

The reactivity of divalent titanium with olefins is of special interest, as they are useful models for probing the mechanics of polymerization. Simple coordination complexes of ethylene

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* Corresponding author. E-mail: sgambaro@science.uottawa.ca. Tel: 613-562-5199. Fax: 613-562-5170.

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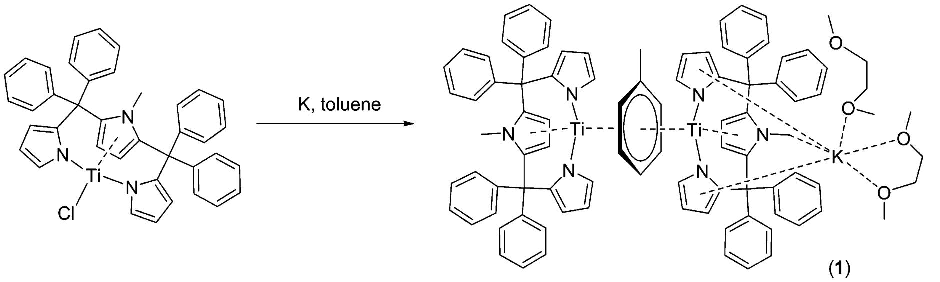
Scheme 1



(**1**)

with low-valent titanium were long believed to be key intermediates in the Ziegler−Natta polymerization process.[8] However, the preparation in the 1980s of the first[9] of the very few existing cases of titanium ethylene complexes[10] has disappointed this expectation, yielding catalytic dimerization rather than polymerization activity. Related to this, the use of bulky aryloxide ligands to support Ti(II) has allowed ethylene coordination and reductive coupling with the *reversible* formation of a titana-cyclopentane ring.[11] This observation is particularly intriguing in light of the fact that the formation of a metallocyclopentane is commonly regarded as the first step in the highly desirable, selective ethylene oligomerization reaction.[12,13] Recent work by Hessen[13] has indicated that an in situ generated divalent Ti may indeed be capable of triggering the catalytic trimerization process with high selectivity.

The judicious choice of ligand system is obviously at the very heart of obtaining highly reactive low-valent titanium species. Incidentally, the work of Hessen has strongly suggested that the use of a hemilabile ligand[13] was beneficial for the Ti-promoted ethylene trimerization, possibly due to its ability to provide sufficient stability to the low-valent center.

Following our interest in the chemistry of low-valent titanium,[14] we have embarked on a project aimed at the preparation of ligand systems based on pyrrolide anions and containing a hemilabile π-system. The use of the pyrrolide anions, which are isoelectronic with the Cp anions, was encouraged by the fact that titanium pyrrolide complexes are known to promote a high catalytic activity for ethylene oligomerization.[15] To this end, we have prepared and fully characterized the $\{2,5\text{-}[(C_4H_3N)CPh_2]_2\ [C_4H_2N(Me)]\}$ dianion, whose central N-methylated pyrrole ring may provide labile π-bonding on demand. Incidentally, this ligand has already been shown to support transient reduced Th species, which are notorious for their extreme reactivity,[16] and has provided active chromium catalysts for ethylene oligomerization.[17]

In the present paper, we describe the use of this particular dianion for the preparation of reduced titanium species. The high reactivity of the low-valent Ti residue is demonstrated in this case by its ability to coordinate and reduce toluene, by providing the first case of coordination of stilbene to a titanium center, and by also cleaving the $CH_3{-}N$ bond of the ligand system.

Results and Discussion

The trivalent LTiCl complex ($L = 2,5\text{-}[(C_4H_3N)CPh_2]_2\text{-}[C_4H_2N(Me)]$), used as a precursor for the reduction reactions

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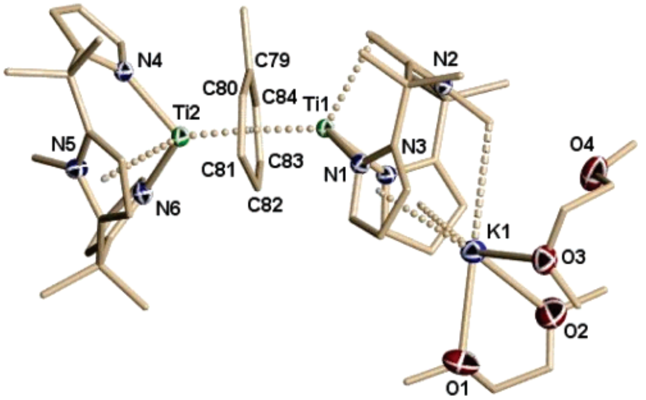

Figure 1. Thermal ellipsoid plot of **1** drawn with ellipsoids drawn at their 50% probability level. Phenyl rings have been omitted for clarity.

described below, was prepared in good yield via a straightforward metathetic reaction between $TiCl_3(THF)_3$ and the dipotassium salt of the ligand in THF.[16] The reduction was performed with K mirror in toluene, affording a dark green, poorly soluble solid. Recrystallization from DME yielded the dinuclear and paramagnetic [LTi(μ_2,η^6-toluene)TiL·K(DME)$_2$] (**1**), which was isolated as dark green crystals in about 50% yield (Scheme 1). The structure of **1** was obtained from an X-ray crystal structure (Figure 1).

The structure of **1** consists of two discrete dinuclear [LTi(μ-C_7H_8)TiL·K(DME)$_2$] units (Table 3) with one molecule of toluene cocrystallized in the lattice. Each of the two titanium atoms is bonded to the tripyrrolide dianion via σ-coordination to the deprotonated pyrrolide rings [Ti(1)−N(1) = 2.195(3) Å, Ti(1)−N(3) = 2.218(3) Å, Ti(2)−N(4) = 2.115(3) Å, Ti(2)−N(6) = 2.145(3) Å]. By adopting the σ-bonding mode, the metal is coplanar with the two rings. The central alkylated pyrrole is orthogonally oriented with respect to titanium and appears to be weakly η^5-coordinated [Ti(1)−N2 = 3.107(5) Å, Ti(1)−C18 = 2.996(4) Å, Ti(1)−C19 = 2.683(4) Å, Ti(1)−C20 = 2.581(4) Å, Ti(1)−C21 = 2.845(4) Å, Ti(1)−centroid = 2.594(4) Å, Ti(2)−N5 = 2.813(5) Å, Ti(2)−C57 = 2.967(4) Å, Ti(2)−C58 = 2.249(4) Å, Ti(2)−C59 = 2.276(4) Å, Ti(2)−C60 = 3.020(4) Å, Ti(2)−centroid = 2.836(5) Å]. The two titanium centers of the dinuclear structure are each η^6-bonded to a side of one molecule of toluene [Ti−centroid = 1.758 and 1.830 Å] in an inverted sandwich-type structure. The two titanium centers are nonequivalent in the sense that one of the two units is coordinated to one potassium, which is in turn solvated by two DME molecules [one dangling and the other fully coordinated K(1)−O(1) = 2.719(4) Å, K(1)−O(2) = 2.741(4) Å, K(1)−O(3) = 2.745(3) Å]. The potassium atom is bonded to the ligand system via π-coordination to the two deprotonated pyrrolide rings, forming K−C distances [3.069(4)−3.274(4) Å] similar to those observed in other pyrrolide-based complexes.[18] There is also an agostic interaction between potassium and the Me group of the central pyrrole ring [K(1)···C(22) = 3.208(4) Å], which is in the range of those detected in [K(Ar)$_2$][M{N(SiMe$_3$)$_2$}$_3$] (M = Mg, Zn)[19] and other potassium salts.[20] The π-bonded bridging molecule of toluene shows a small yet noticeable deviation from planarity [mean deviation from planarity is 0.0484 Å, the largest distortions being at C(81) (0.087 Å from the plane) and C(82) (0.079 Å)]. Similar distortions were also observed in the mononuclear and formally divalent [*N*,*N*′-bis(trimethylsilyl)benzamidinate]Ti(toluene)[21] and (1,2-alternate,Me$_2$Si-bridged-*p*-*tert*-butylcalyx[4]arene)Ti[η^6-1,2,4-$C_6H_3(SiMe_3)_3$][22] complexes. The only other existing example of a complex containing an arene moiety between two titanium centers is the formally mixed-valence Ti(I)−Ti(II) cluster [{Ti$_3$(μ_2-I)$_3$[1,3,5-[AlI$_2$(μ_2-I)]$_3$(μ_3,η^6;η^6-C_6H_3)]}Ti(η^6-C_6H_6)],[23] which shows similar deformation of the bridging ring. Interestingly, this is quite different from the behavior of closely related mixed-valence lanthanide complexes, where the coordinated benzene ring does not show any significant deviation from planarity.[24]

The mixed-valence state of Ti in **1** is indicated not only by the connectivity provided by the crystal structure but also by the paramagnetism of the complex, which incidentally rules out that the proximity of K to the Me group might actually be the result of direct metalation. Complex **1** has a room-temperature magnetic moment as expected for an electronic configuration containing only one unpaired electron ($\mu_{eff} = 1.73\ \mu_{BM}$). The magnetic moment is almost temperature-independent and shows only a very minor and steady decrease to $\mu_{eff} = 1.67\ \mu_{BM}$ on cooling to 2.0 K. The ^{1}H NMR spectrum shows the expected broadening of the spectral lines (scattered over a range of 30 ppm) and is structurally uninformative.

The complex might be regarded as either a Ti(II) or Ti(I), although the substantial Ti-to-ring back-bonding renders the oxidation states rather dubious. The noticeable distortion of the bridging toluene ring speaks of a substantial amount of back-bonding, which is possibly more consistent with a higher valent state description. The mixed-valence state and the different oxidation states of the two metal centers are reflected in the asymmetry of bond distances and angles formed by each of the two Ti atoms with the bridging toluene of the inverse sandwich structure. The asymmetry of the structure of **1** is rather puzzling and initially suggested to us that a potassium-free symmetrical structure formally bearing Ti(II) centers could perhaps be prepared if the stoichiometry of the reductant was adjusted accordingly. To our surprise however, we found that reduction carried out with either smaller or larger amounts of reductants gave only complex **1**, albeit in lower yield. DFT calculations on a model complex (benzene instead of toluene and replacement of the ligand CPh$_2$ groups by CH$_2$ groups) were used to check whether this behavior could be the result of a special stability of the mixed-valence electronic configuration.

The [L′Ti^{II}] fragment was found to have its two d-electrons in orbitals that are mostly d_{xy} and $d_{x^2-y^2}$ in character. These can back-donate into the two benzene π*-orbitals, forming triplet [L′Ti(C_6H_6)]. Combining two [L′Ti^{II}] fragments around a single benzene molecule (in the geometry observed for complex **1**) results in the combination of each benzene π*-orbital with a d_{xy}-orbital of one Ti atom and a $d_{x^2-y^2}$ on the other Ti, resulting in a closed-shell inverse sandwich complex with two equivalent Ti atoms (C_2 symmetry). If an additional electron is forced upon

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Table 1. Highest MOs for $[L'Ti(\mu\text{-}C_6H_6)TiL']^-$

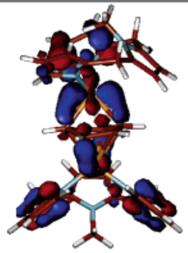
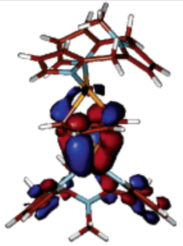
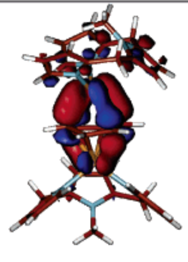
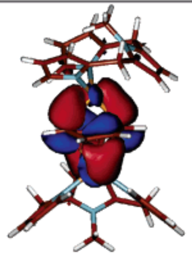
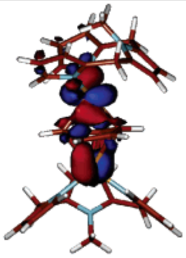
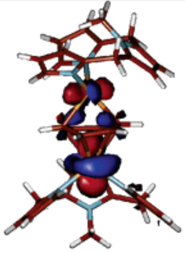
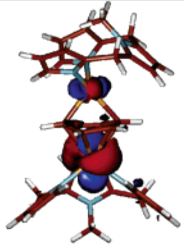
MO	α	β
168		
169		
170		
171		

Table 2. Calculated Benzene Binding Energies of [L′Ti] Fragments (kcal/mol)[a]

reaction	gas phase	toluene (COSMO)	$[(DME)_2K]^+$	$[(DME)_2K]^+$, toluene (COSMO)
$[L'Ti] + C_6H_6 \rightarrow [L'Ti(C_6H_6)]$	−7.3	−6.8		
$[L'Ti] + [L'Ti(C_6H_6)] \rightarrow [L'Ti(\mu\text{-}C_6H_6)TiL']$	−7.1	−3.2		
$2\,[L'Ti(C_6H_6)] \rightarrow [L'Ti(\mu\text{-}C_6H_6)TiL'] + C_6H_6$	+0.2	+3.7		
$[L'Ti]^- + C_6H_6 \rightarrow [L'Ti(C_6H_6)]^-$	−22.1	−20.0	−16.4	−15.4
$[L'Ti]^- + [L'Ti(C_6H_6)]^- \rightarrow [(L'Ti)_2(C_6H_6)]^{2-}$	−7.3	−22.6		
$2\,[L'Ti(C_6H_6)]^- \rightarrow [L'Ti(\mu\text{-}C_6H_6)TiL']^{2-} + C_6H_6$	+14.9	−2.6		
$[L'Ti] + [L'Ti(C_6H_6)]^- \rightarrow [L'Ti(\mu\text{-}C_6H_6)TiL']^-$	−39.4	−32.8	−26.5	−25.2
$[L'Ti(C_6H_6)] + [L'Ti(C_6H_6)] \rightarrow [L'Ti(\mu\text{-}C_6H_6)TiL']^- + C_6H_6$	−32.1	−26.0	−19.2	−18.4

[a] b3-lyp/TZVPP values at b3-lyp/SV(P) geometries. Not corrected for ZPE or thermal effects.

the complex, it goes into a d_{xz}-orbital of *one* of the Ti atoms (Figure 2A shows the spin density, which is clearly concentrated on the top Ti atom). This could be expected to result in a concentration of negative charge on that Ti atom. However, the reduction of one Ti center induces a shift of electron density within the Ti−π*−Ti′ bonding orbitals toward the other Ti atom (most clearly seen in orbital β168, Table 1), to the extent that the final Ti d-orbital populations are virtually identical. The overall result is a binuclear radical anion with complete *spin localization* but full *charge delocalization.* Having the $[(DME)_2K]^+$ cation present makes little difference. The spin density is concentrated on the Ti atom closest to K (Figure 2B), but the two Ti 3d populations still come out equal. Apparently, the presence of the cation does not disturb the charge-delocalized nature of the anion at all. However, the disappearance of the overall negative charge lowers the Ti 3d levels and results in

Table 3. Crystallographic Data and Structure Refinement Details for 1 and 2

	1	**2**
empirical formula	$C_{100}H_{98}KN_6O_4Ti_2$	$C_{56}H_{50}KN_3O_2Ti$
M_r	1582.74	883.99
temp [K]	200(2)	200(2)
radiation used (λ [Å])	Mo Kα (0.71073)	Mo Kα (0.71073)
cryst size [mm]	0.35 × 0.20 × 0.15	0.20 × 0.15 × 0.10
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2(1)$
a [Å]	14.919(5)	12.50(2)
b [Å]	17.276(6)	9.136(16)
c [Å]	18.578(7)	20.49(3)
α [deg]	105.737(6)	90
β [deg]	102.825(6)	101.51(3)
γ [deg]	107.977(6)	90
V [Å^3]	4132(3)	2293(7)
Z	2	2
ρ_{calcd} [g·cm^{-3}]	1.272	1.280
μ [mm^{-1}]	0.301	0.323
$F(000)$	1670	928
scan range θ [deg]	1.33 to 24.79	1.66 to 24.80
no. of total reflns	38 007	16 686
no. of unique reflns	14 074	7740
R(int)	0.0479	0.0378
no. of data/restrains/ params	14 074/15/999	7740/1/569
goodness-of-fit on F^2	1.039	1.003
R_1, wR_2 [$I > 2\sigma(I)$]^a	0.0625 and 0.1510	0.0527 and 0.1226
R_1, wR_2 (all data)^a	0.0986 and 0.1707	0.0690 and 0.1322
max./min. electron dens [e·Å^{-3}]	0.544 and −0.321	0.524 and −0.232

[a] $wR_2 = (\sum[w(F_o^2 - F_c^2)^2]/\sum[F_o^4])^{1/2}$, $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, for **1** weight $= 1/[\sigma^2(F_o^2) + (0.0807P)^2 + (3.7360P)]$, where $P = (\max(F_o^2, 0) + 2F_c^2)/3$; for **2** weight $= 1/[\sigma^2(F_o^2) + (0.0694P)^2 + (1.5336P)]$, where $P = (\max(F_o^2, 0) + 2F_c^2)/3$.

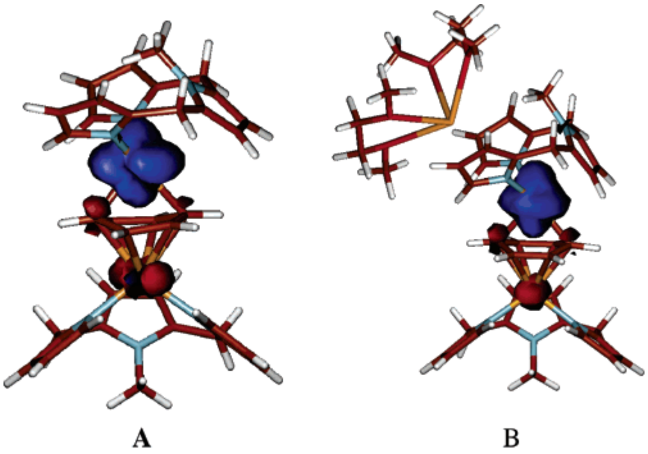


Figure 2. Spin density plots for [L′Ti(μ-C_6H_6)TiL′]$^-$ (A) and [L′Ti(μ-C_6H_6)TiL′·K(DME)$_2$] (B).

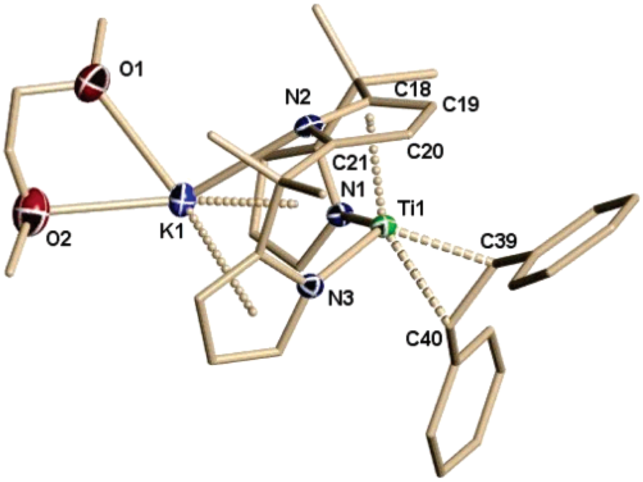


Figure 3. Thermal ellipsoid plot of **2** drawn with ellipsoids drawn at their 50% probability level. Phenyl rings have been omitted for clarity.

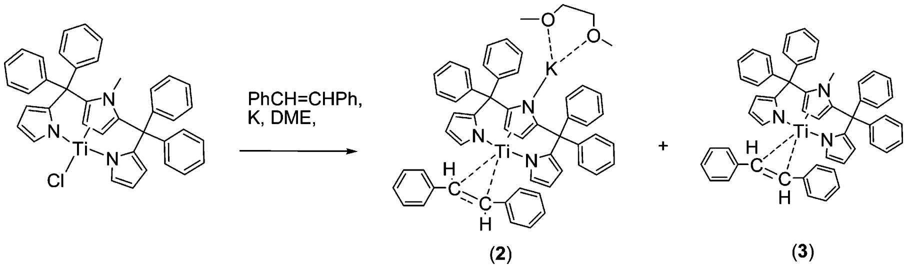
Table 4. Selected Bond Distances (Å) and Angles (deg)

1	**2**
Ti(1)−N(1) = 2.195(3)	Ti(1)−N(1) = 2.059(4)
Ti(1)−N(3) = 2.218(3)	Ti(1)−N(3) = 2.059(4)
Ti(1)−C(82) = 2.208(4)	Ti(1)−C(39) = 2.149(5)
Ti(1)−C(83) = 2.306(4)	Ti(1)−C(40) = 2.205(5)
Ti(1)−C(80) = 2.307(4)	Ti(1)−N(2) = 2.318(4)
Ti(1)−C(79) = 2.347(4)	Ti(1)−C(18) = 2.325(5)
Ti(1)−C(81) = 2.353(4)	Ti(1)−C(21) = 2.403(5)
Ti(1)−C(84) = 2.394(4)	Ti(1)−C(19) = 2.417(6)
Ti(2)−N(4) = 2.115(3)	Ti(1)−C(20) = 2.448(5)
Ti(2)−N(6) = 2.145(3)	
Ti(2)−C(81) = 2.189(4)	N(1)−Ti(1)−N(3) = 107.62(17)
Ti(2)−C(83) = 2.222(4)	N(1)−Ti(1)−C(39) = 111.91(18)
Ti(2)−C(84) = 2.238(4)	N(3)−Ti(1)−C(39) = 117.68(15)
Ti(2)−C(82) = 2.300(4)	N(1)−Ti(1)−C(40) = 97.33(17)
Ti(2)−C(80) = 2.300(4)	N(3)−Ti(1)−C(40) = 91.20(16)
Ti(2)−C(79) = 2.326(4)	C(39)−Ti(1)−C(40) = 38.67(18)
K(1)−O(1) = 2.719(4)	N(1)−Ti(1)−N(2) = 80.92(16)
K(1)−O(3) = 2.745(3)	N(3)−Ti(1)−N(2) = 86.57(14)
	C(39)−Ti(1)−N(2) = 144.74(16)
N(1)−Ti(1)−C(82) = 95.18(14)	C(40)−Ti(1)−N(2) = 176.59(14)
N(1)−Ti(1)−N(3) = 89.01(11)	
N(4)−Ti(2)−N(6) = 98.64(12)	
N(6)−Ti(2)−C(82) = 96.66(13)	
Ti(1)−C(82)−Ti(2) = 105.48(16)	

more extensive mixing with the pyrrole anion π-levels; this makes the final orbital picture (Table S1) less clear. A single [L′Ti^{II}] fragment binds fairly weakly to a benzene molecule. The calculated binding energy is only about 7 kcal/mol, which is hardly enough to keep the complex together in solution. After the addition of a second [L′Ti^{II}] fragment to the other side of the benzene center [Ti(1)−N(1) = 2.059(4) Å, Ti(1)−N(3) = 2.059(4) Å] the binding becomes much more significant. The central pyrrolide ring is now much more strongly π-bonded to titanium [Ti(1)−centroid = 2.060 Å] and σ-bonding to the ring yields an additional 7 kcal/mol. Apparently, the two interactions are not synergistic, which is hardly surprising, considering that both result in Ti→benzene charge transfer. Thus, the combination of two [L′Ti^{II}(C_6H_6)] molecules to [L′Ti^{II}(μ-C_6H_6)Ti^{II}L′] and free benzene is virtually thermoneutral. A hypothetical *anionic* [L′Ti^{I}]$^-$ fragment binds much more strongly to benzene, by ca. 22 kcal/mol. Back-donation from the negative Ti center is much stronger and allows the negative charge to be spread out over the larger size of the complex anion. Complexation of a second [L′Ti^{I}]$^-$ fragment to the same benzene ring is much less exothermic: there will still be extensive Ti→benzene back-donation, but the formation of a dianion is a strongly destabilizing factor. Thus, combination of two [L′Ti^{I}(C_6H_6)]$^-$ anions to [L′Ti^{I}(μ-C_6H_6)Ti^{I}L′]$^{2-}$ and free benzene is *endo*thermic by about 15 kcal/mol. However, coordination of a *neutral* [L′Ti^{II}] fragment to anionic [L′Ti^{I}(C_6H_6)]$^-$ is highly exothermic (by 39 kcal/mol), because it allows for spreading of the negative charge over the two Ti centers. Thus, the single negative charge appears to be a key ingredient in the stability of the complex. Inclusion of a solvent correction (COSMO) and/or an explicit [(DME)$_2$K]$^+$ cation does not change the picture significantly. The effects of the negative charge concentration are attenuated, but formation of the binuclear monoanion remains the most favorable reaction.

Thus, the thermodynamic stability of the mixed-valent **1** appears to be responsible for the lack of formation of a symmetrical structure with the formal appearance of a divalent Ti complex. The dinuclear structure is likely to be preserved in

Scheme 2



solution given that we could not find evidence for exchange of the coordinated toluene with d_8-toluene or d_6-benzene in the normally reachable temperature range. Furthermore, cryoscopic determination of molecular weight in benzene solution afforded values in reasonable agreement with the proposed formulation. These observations have prompted similar reductions in the presence of olefins as trapping agents. Even though back-bonding from the Ti(II) center to the olefin was anticipated, the strange electron coupling, occurring via population of the π^*-system of a bridging toluene and consequent formation of the mixed-valent species, was unlikely to occur in the case of a simple coordinated olefin.

Regrettably, reduction under ethylene gave only intractable materials. However, reduction carried out with 1 equiv of K in the presence of *trans*-stilbene afforded two different diamagnetic compounds, which were isolated and purified by fractional crystallization in DME. The two new species were identified as the dark green $\{2,5\text{-}[(C_4H_3N)CPh_2]_2[C_4H_2N]\}Ti(\eta^2$-*trans*-PhHC═CHPh)[K(DME)] (**2**) and brown $\{2,5\text{-}[(C_4H_3N)CPh_2]_2\text{-}[C_4H_2N(Me)]\}Ti(\eta^2$-*trans*-PhHC═CHPh) (**3**) (Scheme 2).

The structure of **2** (Figure 3) consists of a Ti atom coordinated to a tripyrrrolide, which, having lost the N−Me group, is now trianionic. One molecule of *trans*-stilbene is π-coordinated to the metal center, and one potassium atom, which is solvated by a molecule of DME [K(1)−O(1) = 2.713(6) Å, K(1)−O(2) = 2.809(5) Å], is also part of the structure. The ligand system surrounding Ti adopted the same bonding mode as in **1**, with two deprotonated pyrrolide rings coplanar and σ-bonded to the Ti center [Ti(1)−N(1) = 2.059(4) Å, Ti(1)−N(3) = 2.059(4) Å]. The central pyrrolide ring, which has lost its N−Me group, is π-bonded to titanium [Ti(1)−centroid = 2.060 Å] and σ-bonded to the potassium atom [K(1)−N(2) = 2.873(5) Å]. In turn, the potassium atom is also π-bonded to the two lateral pyrrolide rings [K(1)−centroid = 2.907 and 3.129 Å]. The coordination sphere of the titanium center is completed by one molecule of *trans*-stilbene, which adopts the expected side-on coordination mode [Ti(1)−C(39) = 2.149(5) Å, Ti(1)−C(40) = 2.205(5) Å].

Complex **2** gave the expected NMR pattern in agreement with the X-ray structure with two sets of pyrrolide signals and clearly showing the absence of the N−Me group. The olefinic protons of the π-coordinated stilbene gave only one resonance at 4.85 ppm in the case of **2** and two distinct resonances coupled to each other at 5.05 and 4.77 ppm in the case of **3**. This difference is a possible result of a diminished fluxional behavior caused by the absence of potassium. These chemical shifts fall in the same range of those observed for stilbene complexes of Pt[25] and Ni,[26] although the elongation of the olefinic C−C distance is more pronounced in the case of **2** [C(39)−C(40) = 1.443(6) Å] as a probable result of an increased extent of back-bonding. However, the spectral similarities suggest that the elongations of the stilbene double bond in **2** and **3** are probably comparable. The NMR spectrum of **3** also clearly diagnosed the presence of the N−Me group. Both species can be regarded as either Ti(II)- or Ti(IV)-containing complexes depending on how the extent of back-bonding is being considered. Given the structural similarities to the late metal complexes cited above,[24−26] it is tempting to conclude that the divalent state configuration is predominant in this case.

Conclusions

In this work, we have shown that the tripyrrole dianion $\{2,5\text{-}[(C_4H_3N)CPh_2]_2[C_4H_2N(Me)]\}^{2-}$, with its π-bonded central pyrrole ring, is indeed effective at stabilizing low-valent titanium, as illustrated by the isolation of two olefin complexes and one mixed-valent arene complex. The central pyrrole ring does not coordinate strongly to Ti in **1**, but shows a much stronger Ti−ring interaction in **2**, where due to abstraction of the methyl group, the central ring also became anionic. However, coordination of olefin was still possible when the ligand remained intact, as in the case of **3**. The path leading to loss of the methyl group in **2** is unclear. It might be that the strength of potassium as a reducing agent was also capable of severing the N−Me bond of the coordinated ligand. Indeed, we found that the yield of **2** could be substantially increased by increasing the amount of potassium employed in the reduction. In any event, the presence of methane and ethane in the reaction mixture suggests that a radical pathway is followed during the C−N bond cleavage. Although this type of metal-promoted C−N cleavage has been observed in the case of reduced Th complexes,[16] to the best of our knowledge it is unprecedented in the case of Ti. The attribution of the oxidation state is of course inconclusive in the presence of a π-bonded ligand since it is affected by the extent of back-bonding, as is clearly visible in both **1** and **2**. Nonetheless, the isolation of these species speaks for the possibility of forming genuine low-valent complexes at least as transient intermediates similar to the case of the very useful "Cp_2Ti" synthons. A broader investigation on the chemical reactivity of reduced Ti complexes of the tripyrrolide dianion is in progress.

Experimental Section

All operations were performed under an atmosphere of dry, O_2-free N_2 employing both Schlenk line techniques and a Vacuum Atmospheres inert atmosphere glovebox. Solvents were dried by using an aluminum oxide solvent purification system. Potassium (Aldrich, 99%) and *trans*-stilbene (Aldrich, 99%) were used as received. $TiCl_3(THF)_3$ was prepared by extraction of commercially available $TiCl_3$ (Aldrich, 99%) with boiling THF. The N-alkylated tripyrrole $2,5\text{-}[(C_4H_3NH)CPh_2]_2C_4H_2N(Me)$ ligand[16] was synthe-

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[25] Wicht, D. K.; Zhuravel, M. A.; Gregush, R. V.; Glueck, D. S. *Organometallics* **1998**,*17*, 1412, and references therein.

[26] Brunker, T. J.; Blank, N. F.; Moncarz, J. R.; Scriban, C.; Anderson, B. J.; Glueck, D. S.; Zakharov, L. N.; Golen, J. A.; Sommer, R. D.; Incarvito, C. D.; Rheingold, A. L. *Organometallics* **2005**, *24*, 2730.

sized according to literature procedures. NMR spectra were recorded on a Varian Inova 500 MHz spectrometer. Proton and ^{13}C NMR shifts are reported in δ units downfield from Me_4Si with the solvent as the reference signal. NMR samples were prepared in sealed 5 mm thick walled NMR tubes. Elemental analysis was performed on a Perkin-Elmer 2400 CHN analyzer. Infrared spectra were recorded on a ABB Bomem FT-IR instrument from Nujol mulls prepared in a glovebox. Samples for magnetic susceptibility measurements were weighed inside a glovebox equipped with an analytical balance and sealed into calibrated tubes. The measurements were carried out with a Quantum Design MPMS5S SQUID magnetometer from rt to 2 K. Magnetic moments were calculated following standard methods, and corrections for underlying diamagnetism were applied to the data. X-ray fluorescence analysis was carried out using a Philips PW 2400 spectrometer.

Preparation of {2,5-[(C_4H_3N)CPh_2]$_2C_4H_2N$(Me)}TiCl·(toluene). A solution of 2,5-[(C_4H_3NH)CPh_2]$_2C_4H_2N$(Me) (3.0 g, 5.5 mmol) in THF (30 mL) was treated with KH (0.44 g, 11 mmol) and stirred for 3 h. Addition of $TiCl_3(THF)_3$ (2.05 g, 5.5 mmol) to the solution turned the color of the mixture dark green. Stirring was continued overnight, affording a dark green solution. The solvent was removed in vacuum, and the residue was resuspended in toluene (80 mL). The major part of the solid dissolved, and a white solid was deposited overnight. The mixture was centrifuged to remove a small amount of colorless solid, forming a dark green solution. The solution was concentrated in vacuum to a volume of approximately 5−7 mL and layered with hexane (20 mL). Cystalline olive-green solid was thus formed, which was filtered, washed with hexane (3 × 5 mL), and dried in vacuum for 2 h (3.2 g, 5.1 mmol, 93%). EI-MS: *m*/*z* (%) = 624 (2) [M$^+$]. Anal. Calcd (Found) for $C_{46}H_{39}N_3TiCl$: C 77.04 (76.91), H 5.48 (6.40), N 5.86 (5.79). IR (KBr, cm^{-1}, Nujol mull) ν: 1598 (m), 1582 (sh), 1523 (w), 1488 (s), 1253 (m), 1231 (m), 1214 (sh), 1185 (w), 1146 (w), 1156 (w), 1137 (s), 1131 (s), 1113 (s), 1095 (w), 1083 (m), 1047 (s), 1034 (m), 1002 (w), 990 (w), 957 (w), 929 (w), 913 (w,), 903 (w), 889 (w), 864 (w), 849 (w), 841 (w), 829 (w), 813 (s), 792 (w), 759 (s), 742 (s), 729 (vs), 721 (vs), 701 (vs), 676 (w), 670 (m), 655 (m), 640 (m), 616 (m), 568 (w), 542 (w), 512 (w), 497 (w), 475 (m), 435 (s), 400 (m), 361 (m). ^{1}H NMR (500 MHz, C_6D_6, rt): δ_H (ppm) 43.1 ($\Delta\omega_{1/2}$ 2650 Hz), 7.34 (m, phenyl), 7.27 (d, phenyl), 7.16 (m, phenyl), 7.12 (m, phenyl), 7.05 (m, phenyl), 6.89 (m, phenyl), 6.38 (m, pyrrole), 6.28 (m, pyrrole), 6.25 (m, pyrrole), 5.80 (br s, pyrrole), 5.6 (m, pyrrole), 2.31 (m, pyrrole), −0.94 ($\Delta\omega_{1/2}$ 147 Hz), −11.1 ($\Delta\omega_{1/2}$ 1137 Hz), −20.3 ($\Delta\omega_{1/2}$ 834 Hz) [$\mu_{eff} = 1.81\ \mu_{BM}$ at 24 °C].

Preparation of {2,5-[(C_4H_3N)CPh_2]$_2$[C_4H_2N(Me)]}Ti(μ,η^6-C_7H_8)Ti[{2,5-[(C_4H_3N)CPh_2]$_2$[C_4H_2N (Me)]}][K(DME)$_2$]·toluene (1). Metallic potassium (0.054 g, 1.4 mmol) was heated inside an evacuated flask to form the mirror. Upon cooling to room temperature, anhydrous toluene (10 mL) and {2,5-[(C_4H_3N)CPh_2]$_2$-[C_4H_2N(Me)]}TiCl·toluene (0.70 g, 0.98 mmol) were added. The suspension was stirred for 2 days until complete disappearance of potassium. The resulting dark green suspension was centrifuged and separated from the supernatant liquid. DME (15 mL) was added to the suspension, and the resulting solution was centrifuged again. The dark solution was separated, concentrated to ca. 2−3 mL, and left undisturbed for 4 days at room temperature. Dark green crystals of **1** (0.36 g, 0.23 mmol, 50%) that deposited were separated by filtration, washed with hexane, and dried in vacuum. Anal. Calcd (Found) for $C_{100}H_{98}KN_6Ti_2O_4$: C 75.82 (75.61), H 6.19 (6.20), N 5.31 (5.39). IR (KBr, cm^{-1}, Nujol mull) ν: 1599 (m), 1582 (sh), 1491 (s), 1345 (w), 1322 (w), 1295 (m), 1285 (sh), 1258 (s), 1223 (s), 1208 (w), 1193 (sh), 1184 (m), 1150 (s), 1141 (s), 1124 (w), 1109 (s), 1085 (vs), 1073 (s), 1047 (s), 1036 (sh), 1019 (m), 1003 (w), 980 (s), 973 (s), 945 (w), 932 (s), 921 (sh), 898 (m), 874 (m), 866 (w), 854 (m), 848 (m), 792 (m), 764 (vs), 742 (vs), 725 (vs), 716 (vs), 697 (vs), 670 (s), 659 (m), 649 (w), 635 (m), 627 (s), 611 (w), 605 (w), 550 (w), 527 (w), 486 (m), 465 (w), 441 (w), 418 (m), 407 (m), 373 (m). ^{1}H NMR (500 MHz, C_6D_6, rt) δ (ppm): 27 (v br), 21 (v br, overlapped with the resonance at 27 ppm), 7.19 (m, toluene, overlapped with the broad resonance), 7.12 (m, toluene, overlapped with the broad resonance), 6.3 ($\Delta\omega_{1/2}$ = 131 Hz), 3.43 (−C*H*$_2$−, $\Delta\omega_{1/2}$ = 1.9 Hz, DME), 3.14 (−C*H*$_3$, $\Delta\omega_{1/2}$ = 1.9 Hz, DME), 2.31 (−C*H*$_3$, $\Delta\omega_{1/2}$ = 2.5 Hz, toluene), −3.7 ($\Delta\omega_{1/2}$ = 355 Hz) [$\mu_{eff} = 1.67\ \mu_{BM}$ at 24 °C].

Preparation of {2,5-[(C_4H_3N)CPh_2]$_2$[C_4H_2N]}Ti(η^2-*trans*-PhHC═CHPh)[K(DME)] (2) and {2,5-[(C_4H_3N)CPh_2]$_2$[C_4H_2N-(Me)]}Ti(η^2-*trans*-PhHC═CHPh) (3). A suspension of {2,5-[(C_4H_3N)CPh_2]$_2$[C_4H_2N(Me)]}TiCl·toluene (0.64 g, 0.91 mmol) and potassium (0.50 g, 1.3 mmol) in DME (7 mL) was vigorously stirred in the presence of *trans*-stilbene (018 g, 1.0 mmol). The initially green suspension slowly dissolved within 2−3 h, affording a dark green solution, which eventually gave a brown suspension. Once potassium was completely consumed, the dark brown mixture was centrifuged. The supernatant DME solution was concentrated and allowed to stand at −30 °C for 4 days, upon which green crystals of **2** formed (0.20 g, 0.23 mmol, 25%). The brown solid residue obtained from the centrifugation was mixed with 15 mL of toluene, stirred, and centrifuged, thus affording a clear dark brown suspension. After further centrifugation, the supernatant was separated from the insoluble solid. Extraction of the insoluble solid with toluene was repeated four times. The toluene extracts were combined, concentrated to 3−4 mL, and allowed to stand at −30 °C for 4 days. During this time a brown solid of **3** deposited (0.20 g, 0.26 mmol, 30%), which was separated by filtration, washed with hexane, and dried in a vacuum.

Compound 2. Anal. Calcd (Found) for $C_{56}H_{50}KN_3TiO_2$: C 76.02 (76.00), H 5.66 (5.68), N 4.75 (4.76). IR (KBr, cm^{-1}, Nujol mull) ν: 1587 (m), 1485 (s), 1301 (m), 1274 (w), 1262 (w), 1247 (m), 1226 (m), 1220 (sh), 1180 (w), 1172 (m), 1144 (s), 1135 (s), 1109-(m), 1079 (m) 1069 (w), 1041 (s), 1003 (w), 996 (w), 983 (m), 955 (w), 927 (m), 900 (m), 876 (w), 853 (m), 830 (m), 790 (m), 772 (sh), 760 (vs), 740 (vs), 728 (vs), 698 (vs), 656 (m), 644 (m), 626 (m), 619 (w), 610 (w), 563 (w), 548 (w), 532 (w), 516 (m), 504 (w), 488 (m), 465 (w), 449 (m), 417 (m), 412 (m), 394 (w). ^{1}H NMR (500.2 MHz, C_6D_6, rt): δ_H (ppm) 7.81 (m, 4H, C$_6$*H*$_5$), 7.57 (dd, 1H, J_{AC} = 1.2 Hz, J_{AB} = 2.4 Hz, C$_4$*H*$_3$N (1)), 7.42 (m, 2H, C$_6$*H*$_5$), 7.34−7.03 (m, 22H, C$_6$*H*$_5$), 6.81 (t, 2H, *J* = 6.6 Hz, C$_6$*H*$_5$), 6.15 (dd, 1H, J_{AC} = 1.2 Hz, J_{BC} = 2.4 Hz, C$_4$*H*$_3$N (1)), 6.11 (t, 1H, J_{AB} = J_{BC} = 2.4 Hz, C$_4$*H*$_3$N (1)), 5.77 (dd, 1H, J_{AC} = 1.3 Hz, J_{AB} = 3.0 Hz, C$_4$*H*$_3$N (2)), 5.75 (d, 1H, *J* = 2.5 Hz, C$_4$*H*$_2$-NMe), 5.70 (dd, 1H, J_{AC} = 1.3 Hz, J_{BC} = 2.4 Hz, C$_4$*H*$_3$N (2)), 5.35 (t, 1H, J_{AB} = 3.0 Hz, J_{BC} = 2.4 Hz, C$_4$*H*$_3$N (2)), 4.85 (s, 2H, PhC*H*C*H*Ph, stilbene), 4.04 (d, 1H, *J* = 2.5 Hz, C$_4$*H*$_2$NMe), 3.34 (s, 4H, C*H*$_2$−, DME), 3.13 (s, 6H, −C*H*$_3$, DME). ^{13}C−^{1}H HMQC (ppm): 130.1 (7.42, C$_6$*H*$_5$), 129.8 (7.31, 7.29, 7.26, C$_6$*H*$_5$), 129.7 (7.34, C$_6$*H*$_5$), 129.6 (7.82, 7.79, C$_6$*H*$_5$), 129.3 (7.13, 7.10, C$_6$*H*$_5$), 128.1 (7.19, 7.16, C$_6$*H*$_5$), 127.4 (7.24, C$_6$*H*$_5$), 128.8−126.6 (7.06−7.0, C$_6$*H*$_5$), 122.6 (7.57 (C$_4$*H*$_3$N (1)), 121.4 (6.81, C$_6$*H*$_5$), 117.0 (4.04, C$_4$*H*$_2$NMe), 112.9 (5.70, C$_4$*H*$_3$N (2)), 110.8 (5.77, C$_4$*H*$_3$N (2)), 108.0 (6.15, C$_4$*H*$_3$N (1)), 107.0 (5.75, C$_4$*H*$_2$NMe), 104.1 (6.11, C$_4$*H*$_3$N (1)), 102.7 (5.35, C$_4$*H*$_3$N (2)), 101.9 (4.85, PhC*H*C*H*Ph), 72.0 (3.34, DME), 58.6 (3.13, DME).

Compound 3. Anal. Calcd (Found) for $C_{53}H_{43}N_3Ti$: C 82.71 (82.67), H 5.59 (5.49), N 5.46 (5.47). The X-ray fluorescence spectrum showed no chlorine in **3** and a small amount of potassium (<0.5%) attributed to the presence of impurities of **2**. IR (KBr, cm^{-1}, Nujol mull): ν 1590 (m), 1302 (w), 1275 (w), 1260 (m), 1247 (m), 1222 (m), 1183 (w), 1173 (w), 1163 (w), 1144 (s), 1132 (vs), 1114 (s), 1106 (s), 1089 (m), 1082 (m), 1070 (m) 1045 (s), 1031 (m), 1003 (w), 992 (m), 986 (m), 957 (w), 935 (m), 916 (w), 902 (m), 894 (w), 868 (w), 851 (w), 838 (m), 794 (m), 777 (m), 762 (s), 743 (vs), 729 (vs), 717 (s), 696 (vs), 678 (w), 655 (m), 645 (m), 616 (m), 606 (w), 559 (w), 547 (w), 528 (m), 516 (m), 482 (m), 458 (w), 442 (w), 425 (m) 385 (w). ^{1}H NMR (500 MHz, C_6D_6, rt): δ_H (ppm) 7.96 (dd, 1H, $J_{AC} = 0.7$ Hz, $J_{AB} = 2.6$ Hz, C_4H_3N (1)), 7.59 (br, 3H, C_6H_5 of stilbene), 7.38 (br, 2H, C_6H_5 of stilbene), 7.35 (m, 2H, C_6H_5), 7.28, (m, 4H, C_6H_5), 7.19−6.95 (m, 14H, C_6H_5), 6.85 (dd, 1H $J_{AC} = 0.7$ Hz, $J_{BC} = 3.2$ Hz, C_4H_3N (1)), 6.74 (br, 2H, C_6H_5 of stilbene), 6.71 (t, 1H, $J_{AB} = 2.6$ Hz, $J_{BC} = 3.2$ Hz, C_4H_3N (1)), 6.61 and 6.55 (br, 3H, C_6H_5 of stilbene, overlapped resonances), 6.38 (dd, 1H, $J_{AB} = 2.7$ Hz, J_{AC} 0.8 Hz, C_4H_3N (2)), 6.12 (dd, 1H, $J_{BC} = 2.4$ Hz, $J_{AC} = 0.8$ Hz, C_4H_3N (2)), 5.89 (t, 1H, $J_{AB} = 2.7$ Hz, $J_{BC} = 2.4$ Hz C_4H_3N (2)), 5.19 (d, 1H, $J = 3.4$ Hz, C_4H_2NMe), 5.05 (d, 1H, $J = 12$ Hz, stilbene PhC*H*CHPh,), 4.77 (d, 1H, $J = 12$ Hz, stilbene PhCHC*H*Ph,), 3.79 (d, 1H, $J = 3.4$ Hz, C_4H_2NMe), 3.54 (s, 4H, $-CH_2$ of DME), 3.15 (s, 6H $-CH_3$ of DME), 2.06 (s, 3H, C_4H_2NMe). $^{13}C-^1H$ HMQC (ppm): 124.8 (7.96 C_4H_3N (1)), 130.0 (7.35, C_6H_5), 129.9 (7.28, C_6H_5), 129.2 (7.11, C_6H_5), 128.4 (7.08, 7.07, 6.99, C_6H_5), 128.2 (7.04, C_6H_5), 128.0 (7.19, C_6H_5), 126.8 (6.12, C_4H_3N (2)), 126.7 (6.96, C_6H_5), 110.3 (3.79, C_4H_2NMe), 110.2 (4.77, PhCHC*H*Ph), 109.9 (6.85, C_4H_3N (1)), 109.1 (5.19, C_4H_2NMe), 106.3 (6.71, C_4H_3N (1)), 108.2 (6.38, C_4H_3N (2)), 106.1 (5.05, PhC*H*CHPh), 104.5 (5.89, C_4H_3N (2)), 72.0 (3.54, DME), 58.6 (3.15, DME), 35.1 (2.06, C_4H_2NMe).

X-ray Crystallography. Suitable crystals were selected, mounted on a thin, glass fiber with paraffin oil, and cooled to the data collection temperature. Data were collected on a Bruker AXS SMART 1 k CCD diffractometer. For **1** data collection was performed with four batch runs at $\phi = 0.00°$ (650 frames), at $\phi = 90.00°$ (650 frames), at $\phi = 180.00°$ (650 frames), and at $\phi = 270.00°$ (650 frames). For **2** data collection was performed with three batch runs at $\phi = 0.00°$ (650 frames), at $\phi = 120.00°$ (650 frames), and at $\phi = 240.00°$ (650 frames). Initial unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied. The systematic absences and unit-cell parameters were consistent for the reported space groups. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F^2. All non-hydrogen atoms except cocrystallized toluene solvent molecules in the structure of **1** were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are contained in the SHELXTL 6.12 program library.

Complex **1** has one toluene solvent molecule per two titanium atoms in the lattice. This toluene molecule was located in the general position and was disordered over two positions with equal occupancy. Relevant crystal data and bond distances and angles are given in Tables 3 and 4, respectively.

Calculations. In the calculations, the CPh_2 groups connecting the ligand pyrroles were replaced by CH_2 groups; thus the ligand was presented as L′ and the bridging toluene was modeled by benzene. All calculations were carried out with the Turbomole program[27] coupled to the PQS Baker optimizer.[28] Calculations on open-shell systems used the spin-unrestricted formalism. Geometries were fully optimized at the b3-lyp level[29] using the Turbomole SV-(P) basis set [27a,c] on all atoms. Frequency calculations were not feasible for the large binuclear systems, so the energies could not be corrected for ZPE and thermal effects. Improved energies were obtained from single-point calculations at the b3-lyp level[29] using the TZVPP basis.[27] Solvent corrections were calculated at the b3-lyp/TZVPP level using the COSMO solvation model[30] with a dielectric constant of 2.34 (toluene). Orbital drawings were created using Molden.[31] Figure 2 shows the calculated spin density for $[L'Ti(\mu\text{-}C_6H_6)TiL']^-$ and $[L'Ti(\mu\text{-}C_6H_6)TiL'\cdot K(DME)_2]$, Table 1 the highest orbitals for $[L'Ti(\mu\text{-}C_6H_6)TiL']^-$, and Table S1 those for $[L'Ti(\mu\text{-}C_6H_6)TiL'\cdot K(DME)_2]$; Table S2 lists calculated total energies.

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Supporting Information Available: Crystallographic data (CIF) for **1** and **2**, and details of the DFT calculations (including spin density plots) for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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