

Direct Epimetallation of π -Bonded Organic Substrates with Titanium(II) Isopropoxide: Intermediacy of Biradical, Oligomeric Titanium(II) Reagents^[‡]

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Keywords: Titanium(II) / EPR determination of biradicals / Titanium(II) isopropoxide trimer / Epititanation / Nonstereochemical Ti^{II} additions

Extensive EPR experiments show that a titanium-containing molecular triplet state is formed in solution by the reaction of two equivalents of butyllithium with one equivalent of titanium(IV) isopropoxide. At higher concentrations this product, titanium(III) isopropoxide, admixed with two equivalents of lithium isopropoxide, is accompanied by the formation of a variety of nontitanium-containing side products. The powder EPR spectrum of the molecular triplet state in frozen solution is consistent with an asymmetric molecular chain of three Ti centers on which the unpaired electron centers are three metal atoms apart. Dilution experiments show that at lower concentrations, where the nontitanium-containing side products have dissipated, the intensity of the molecular triplet spectrum varies approximately linearly with concentration. Thus there is no evidence that the observed triplet molecule is one component in a series of concentration-dependent oligomerization steps. The bulky isopropoxy substituents and the coordination of the isopropoxide anions from the LiOiPr present appear to prevent closure of the Ti₃ centers into an equilateral triangular diamagnetic structure. This steric hin-

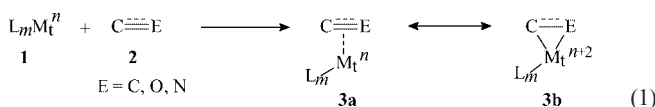
drance, operative at the terminal diisopropoxytitanium centers and preventing closure to a ring, seems not to be observed with TiCl₂·2THF, which is diamagnetic and may thus be expected to exist as an equilateral triangular cluster of three units of TiCl₂·2THF, a structural model currently under further investigation. The smaller steric demand of the chloro and THF units would seem to permit octahedral coordination about each Ti center in such an equilateral trigonal array of Ti₃ atoms. Chemical reactions carried out individually with diphenylacetylene, *cis*-stilbene or *cis*-stilbene oxide and titanium(II) diisopropoxide provide stoichiometric and stereochemical evidence that the attacking titanium(II) reagent is in fact the trimeric biradical. The role of the lithium isopropoxide byproduct in fostering the course of the previously reported SET reactions of titanium(II) isopropoxide and in determining the detailed structure of the open-chain Ti trimer biradical has been explicated.

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Introduction

The complexation of subvalent transition-metal reagents ($L_mM_t^n$, **1**) with various C=C, C≡C, C=O, or C=N linkages (as in **2**) has led to adducts **3** that may be considered as π complexes **3a**, where the metal has undergone little change in oxidation number (M_t^n). On the other hand, the metal center can have released significant electron density to the π^* -orbital of the organic substrate with the formation of three-membered metallocycles **3b**, and the metal may thereby have a higher oxidation number (M_t^{n+2}) [Equation (1)]. To determine which of the resonance structures **3a** and **3b** is the better single structure of adduct **3**, it is neces-

sary to perform individual evaluations of the structural parameters of adduct **3**, if isolated, or of its observed chemical reactions.^[2–4]

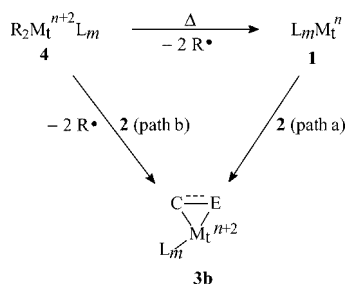


The process involved in the formation of adduct **3** has been termed epimetallation, because the metal reagent **1** is added with the rupture of a π -bond.^[2] If reagent **1** is generated in a separate step and then added to **2**, this process may be termed direct epimetallation (Scheme 1, path a). More recently, however, we have found that a precursor dialkyl derivative of higher oxidation number, $R_2M_t^{n+2}L_m$ (**4**), can itself transfer the $L_mM_t^n$ unit to the unsaturated substrate **2** with concomitant loss of the R groups (Scheme 1, path b). This latter process has accordingly been termed transfer-epimetallation.^[5a, 6]

[‡] Organic Chemistry of Subvalent Transition-Metal Complexes, 38. Part 37: Ref.^[1]

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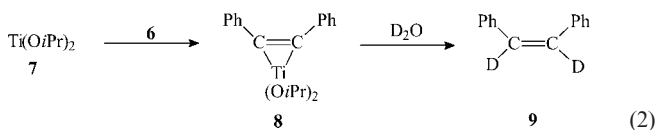
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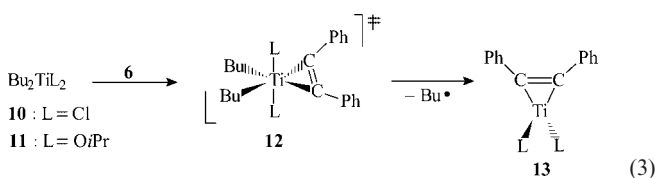
Scheme 1.

It is noteworthy to observe that the epititanation of ethylene by titanium(II) diisopropoxide (**7**) is widely thought to lead to 1,1-diisopropoxy-1-titanacyclopropane, postulated as the key intermediate in the Kulinkovich cyclopropanol synthesis.^[5]

A most unusual and unexpected observation made in comparing such epimetallations with titanium reagents is that the direct epititanations with preformed TiL_2 ($\text{L} = \text{Cl}$, OiPr)₂ are much slower than transfer-epititanations with Bu_2TiL_2 .^[2,5] For example, preformed TiCl_2 (**5**) in THF can achieve no epititanation of diphenylacetylene (**6**) whatsoever at 25 °C; similarly, $\text{Ti}(\text{OiPr})_2$ (**7**) in THF reacts with **6** over 24 h to provide only 31% of the epititanation product **9**, presumed to stem from adduct **8**, which was detected through D_2O cleavage as **9** [Equation (2)]. In considering this low reactivity of TiCl_2 or $\text{Ti}(\text{OiPr})_2$ in direct epititanations, it is still noteworthy that some moderate activity is shown by $\text{Ti}(\text{OiPr})_2$ at 25 °C, while TiCl_2 is completely unreactive. As will be observed later in this study, this distinct difference in the chemical reactivity of $\text{Ti}(\text{OiPr})_2$ vs. TiCl_2 is also reflected in their respective EPR activity.



In sharp contrast, however, when either Bu_2TiCl_2 (**10**) or $\text{Bu}_2\text{Ti}(\text{OiPr})_2$ (**11**) was generated in THF at -78 °C and 0.9 equiv. of diphenylacetylene (**6**) was then added, subsequent warming to 25 °C and treatment with D_2O gave a 91–99% yield of *cis*-[$\text{D}_{1,2}$]stilbene (**9**). This outcome clearly demonstrates that **10** or **11** achieves a rapid epititanation of **6** at or below 25 °C. The facility of such transfer-epititanation has been rationalized by the formation of an octahedral transition state **12** with **6**, in which the new, incipient C–Ti bonds of the epititanated product are formed as the butyl–titanium bonds are thereby predisposed to homolytic cleavage [Equation (3)].



A most likely reason for the greater epititanation activity of Bu_2TiL_2 (**10** or **11**) over that of TiL_2 (**5** or **7**) may well be the more associated character of TiL_2 . In the solid state, it should be noted that the TiCl_2 crystal lattice consists of layers of an infinite plane of Ti atoms flanked on both sides by infinite planes of chlorine atoms. It is understandable that considerable activation energy would be required to generate monomeric TiL_2 units, even from a far less associated form of these titanium(II) salts. As produced from 2 equiv. of butyllithium with 1 equiv. of TiCl_4 or $\text{Ti}(\text{OiPr})_4$, the resulting TiL_2 remains admixed with 2 equiv. of either LiCl or $\text{Li}(\text{OiPr})_2$. The separation of pure TiCl_2 or $\text{Ti}(\text{OiPr})_2$, free of Li salts, for analytical or molecular weight measurements, is a difficult task. We have been able to isolate and analyze successfully $\text{TiCl}_2 \cdot 2\text{THF}$, free of LiCl , but we have been uniformly unsuccessful in separating $\text{Ti}(\text{OiPr})_2$ from LiOiPr , since both components are freely soluble in pure THF or in hexane.

Hindered from determining the degree of association of pure $\text{Ti}(\text{OiPr})_2$ (**7**) in solution, we have availed ourselves of another interesting physical property of **7**. In contrast with the diamagnetic character of TiCl_2 (**5**) in THF over a range of temperatures below 25 °C, we have found that $\text{Ti}(\text{OiPr})_2$ with its byproduct LiOiPr in heptane/toluene solution is pronouncedly paramagnetic and displays an EPR triplet signal characteristic of a biradical. The detailed study of such an EPR spectrum now permits us to estimate the degree of association of such $\text{Ti}(\text{OiPr})_2$ units.^[7] Extrapolating from data on alkali metal complexes of TiCl_2 , such as $\text{Na}_2\text{Ti}_3\text{Cl}_8$, we now suggest a possible similarity in the association of TiCl_2 units in THF.

Results and Discussion

The EPR Investigation of the 1:2 Mixture of Titanium(II) Diisopropoxide (**7**) and Lithium Isopropoxide in 1:1 Solutions of Heptane/Toluene

The initial CW EPR investigation of diluted samples of such mixtures, where the concentration of **7**, formally considered as the monomer, was successively 20.0, 7.0, 2.0, and 0.7 mM, revealed a broad, strong line at $g = 1.944$, a sharp line at $g = 1.964$, and a complex set of lines around $g = 1.98$. Subsequent examination of this flash-frozen sample at 80 K gave a spectrum with a central set of features between 3100 and 3800 Gauss (microwave frequency, $\nu = 9.36947$ GHz) and a weak feature at 1690 Gauss (microwave frequency, $\nu = 9.36583$ GHz). The experiment was repeated with the spin-echo technique at 25 K, which confirmed the CW EPR results. In both cases, the central region appeared to comprise weak wing features at 3150 and 3750 Gauss, shoulders at 3125 and 3575 Gauss, and a peak at 3460 Gauss, relative to $\nu = 9.4181$ GHz. After refinements in sample preparation had been made, the 3150 and 3575-Gauss features were eliminated. Please note the g -value representation of the central region of the spectrum as presented in Figure 1, as the derivative of EPR absorption with respect to the field. An integral (absorption vs.

field) of the EPR spectrum in this region is shown in Figure 2. The low-field part of the EPR spectrum is shown in Figure 3.

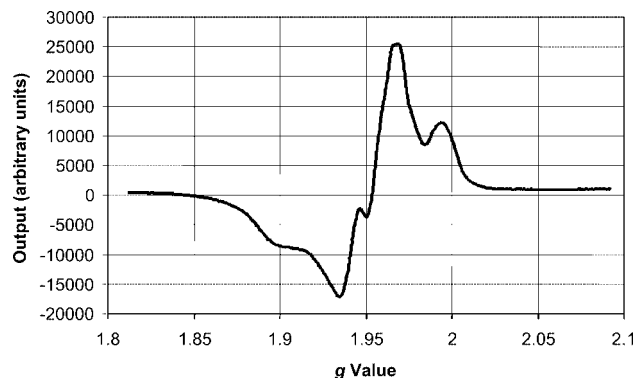


Figure 1. CW EPR derivative spectrum of a 0.7 mm frozen 1:1 hexane/toluene solution of titanium isopropoxide at 50 K as a function of g value in the $g = 2$ region.

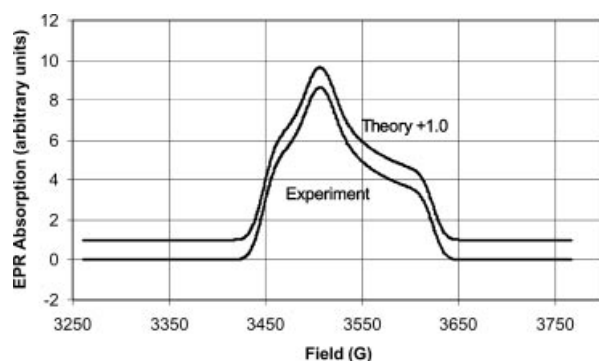


Figure 2. CW EPR absorption spectrum of a 0.7 mm frozen 1:1 hexane/toluene solution of titanium isopropoxide at 50 K, experiment and theory at microwave frequency 9.54971 GHz. (The normal derivative output of the EPR spectrometer has been numerically integrated.)

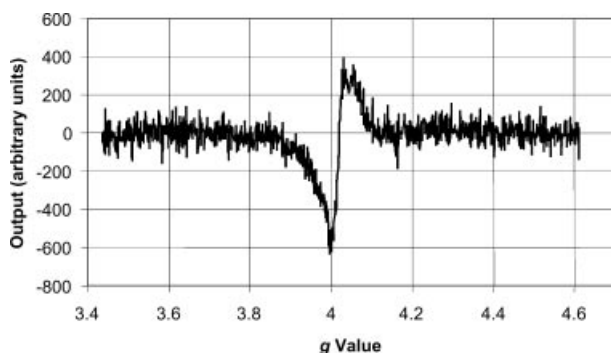


Figure 3. CW EPR derivative spectrum of a 0.7 mm frozen 1:1 hexane/toluene solution of titanium isopropoxide at 50 K as a function of g value in the $g = 4$ region.

Dilution experiments were done in order to try to understand the relationships between the several features observed in the CW EPR solution spectrum (not shown) and to consider the possibility that various oligomers of titanium(II) isopropoxide were being observed. Four sets of dilution experiments at nominal monomeric titanium(II) iso-

propoxide concentrations of 20.0, 7.0, 2.0, and 0.7 mM were done with successively greater refinements in the procedures. The sharp line at $g = 1.964$ observed at 20.0 and 7.0 mM was largely eliminated with this improved procedure. The complex set of weak lines around $g = 1.98$ initially observed at all concentrations except 0.7 mM was eliminated by means of the improved technique at all concentrations except 20.0 mM. The intensity of the triplet signal varies approximately in a linear dependence with the concentration, once the complex at $g = 1.98$ disappears upon dilution.

Analysis of the Observed EPR Spectra of Titanium Diisopropoxide (7)

The central part of the frozen solution spectrum, shown in integral form in Figure 2, is characteristic of a powder pattern of a molecular triplet state. The so-called half-field feature shown in the frozen solution spectrum of Figure 3 is located at a field consistent with a weakly allowed $\Delta m_s = \pm 2$ transition between the levels of a triplet state under the influence of the dipole-dipole interaction of the unpaired triplet-state electrons.^[8] The parameters determined with the following triplet-state spin Hamiltonian [Equation (4)] are given in Table 1.

$$\mathbf{H} = H \cdot g \cdot S + D S_z^2 + E(S_x^2 - S_y^2) \quad (4)$$

Table 1. Spin Hamiltonian parameters obtained from a least-squares fit of the parameters in Equation (4) to the titanium diisopropoxide frozen solution in Figure 2. (The standard deviations σ in the parameters are also presented. The absolute signs of D and E are unknown but their relative signs are opposite.)

	Value	σ
D ($10^{-4} \text{ cm}^{-1} hc$)	± 81.7	1.8
E ($10^{-4} \text{ cm}^{-1} hc$)	∓ 23.1	0.2
g_{xx}	1.9293	0.0002
g_{yy}	1.9449	0.0002
g_{zz}	1.9304	0.0002
ΔH (Gauss)	18.7	0.5

The g value (1.944) of the broad strong line in the solution spectrum (not shown) is the same as that of the triplet molecule. Thus the solution spectrum is believed to be the motionally averaged spectrum of the powder pattern of the triplet molecule observed at lower temperatures (See Figure 2). The relatively smaller g -shift of the complexes giving the variable set of lines at $g = 1.98$ suggests that these are radicals free of a Ti center. In the most highly refined dilution spectra it appears that the only highly concentration-dependent spectrum is that of the non-Ti-containing complex. It would appear that the triplet spectrum associated with Ti at $g = 1.944$ is present at all concentrations and its spectrum does not change appreciably with concentration. Its intensity scales approximately with concentration, once the complex at $g = 1.98$ disappears upon dilution.

Ignoring the E value for the moment, the D value alone corresponds to the dipolar interaction of two point-electron spins on titanium atoms at a distance of 0.668 nm.^[9] Since

this Ti–Ti separation is more than twice the titanium atom separation in the $[\text{Ti}_3]$ cluster found in $\text{Na}_2\text{Ti}_3\text{Cl}_8$, the unpaired electrons are clearly not on the same Ti center or unlikely even on adjacent Ti centers. The nonzero E value rules out a symmetric trigonal (equilateral) array, such as the $[\text{Ti}_3]$ cluster^[10] for which $E = 0$ by symmetry.

Quantitative estimates of the triplet component(s) present in samples with 0.7, 2.0, 7.0, and 20.0 mM Ti content gave an average of 0.28 ± 0.14 triplet spins per Ti atom. Although within one standard deviation such a value is not consistent with triplet spins on the same Ti atom (1.0) or on adjacent Ti atoms (0.50). However, this value is in agreement with three Ti atoms per triplet molecule (0.33). Of course, this value is also consistent with four (0.25), five (0.20), six (0.17), or seven (0.14) Ti atoms per triplet molecule. This outcome supports the conclusion that a determination of the number of Ti atoms per triple molecule, measured with a precision typical of such experiments, cannot by itself be expected to determine the specific number of Ti atoms per Ti cluster.

Comparison of the EPR Data for Titanium(II) Diisopropoxide (**7**) with Various Structural Models

A continuum of titanium(II) isopropoxide oligomers come under consideration (**7a–7d**, arrow = relative orientation of electron spin). From the D and E values, monomer **7a** and diamagnetic trimer **7d** can be excluded from further consideration. From the D values alone the Ti–Ti distance in **7b** (0.2996 nm) is too short, and even a linear trimer of **7c** ($\theta = 180^\circ$) falls short (0.599 nm) of the calculated experimental value of 0.668 nm (see Figure 4). The linear tetramer of **7** would lead to a D value of 0.8988; however, the substantial value of E is not predicted by a range of models reproducing the value of D , including one with parallel p -type orbitals simulated by point spins on terminal Ti atoms, a model with a twist angle between the terminal Ti p -type orbitals, and a model with in-plane p -type point spins and a Ti–Ti–Ti bond angle $\theta = 105^\circ$. This failure in prediction suggests that there may also be one-center dipole–dipole contributions or spin-orbit contributions to the zero-field parameters of Equation (4). The D value and the nonzero E value suggest a structure differing fundamentally in two respects from that of the $[\text{Ti}_3]^{6+}$ cluster found by Hinz et al. in $\text{Na}_2\text{Ti}_3\text{Cl}_8$ at low temperatures.^[10] The D value suggests

a greater average triplet electron separation than the ≤ 0.2996 nm value in the $[\text{Ti}_3]^{6+}$ cluster. The nonzero E value rules out a symmetric trigonal structure, such as was found for the $[\text{Ti}_3]^{6+}$ cluster, for which $E = 0$ by symmetry. Thus, with all factors considered, the structural model most in accord with the EPR data would appear to be **7c**, where θ approaches 180° , and the individual Ti–Ti bonds are lengthened to greater than 0.2996 nm by the steric repulsion of the isopropoxy groups attached to adjacent titanium centers (**7e**, $L = \text{OiPr}$) (See Figure 4). The same steric bulk of the isopropoxy groups would weaken any coordination of THF units to Ti centers, as well as hindering spin-pairing and closure to the symmetrical $[\text{Ti}_3]$ cluster **7f** [Equation (5)].

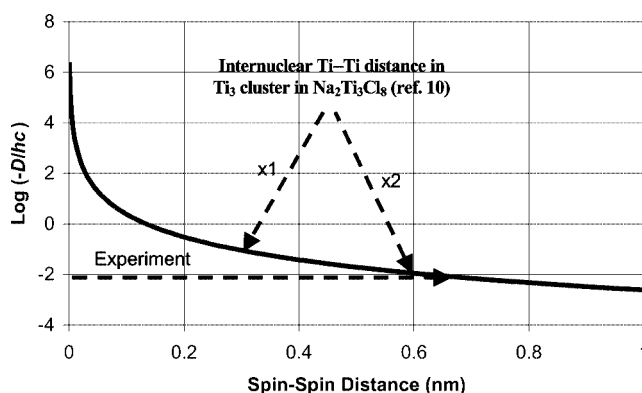
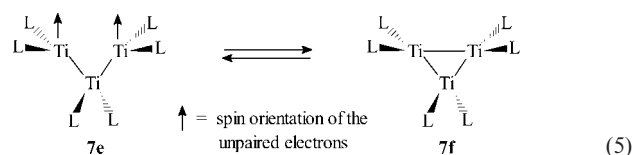
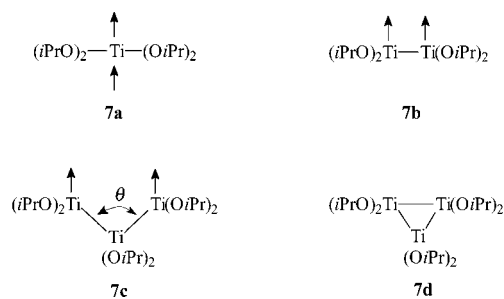


Figure 4. Logarithmic plot of the D values as a function of point-spin-point-spin distance, according to a simple dipole-dipole model placing the spins on terminal Ti atoms. On this plot, the experimentally measured value of D is indicated in relation to multiples of the Ti–Ti internuclear distance in the Ti_3 cluster reported by Hinz and co-workers.^[10]

The tendency of divalent titanium centers to form trimeric Ti clusters, as in the solid state of $\text{Na}_2\text{Ti}_3\text{Cl}_8$ ^[10] and as here in solutions of $\text{Ti}(\text{OiPr})_2$ (**7**), encourages us to suggest that diamagnetic $\text{TiCl}_2 \cdot 2\text{THF}$ (**5**·2THF) may exist in solution as the cyclic symmetrical structure **7f**, ($L = \text{Cl}$), in which each Ti center, because of the smaller, electronegative chlorine ligand, could further accommodate two THF ligands and thereby attain octahedral coordination. The possible existence of cyclic and open-chain trimeric clusters of **7e** and **7f** ($L = \text{Cl}$) will be probed by EPR measurements of $\text{TiCl}_2 \cdot 2\text{THF}$ conducted at higher temperatures.^[11]

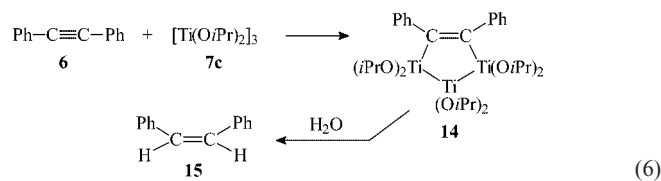
Structure of Titanium(II) Diisopropoxide (**7**) Implied by Its Chemical Reactions

In both $[\text{Ti}(\text{OiPr})_2]_3$ and $[\text{TiCl}_2 \cdot 2\text{THF}]_3$, it is readily apparent that the monomeric TiL_2 unit, necessary for the epi-



titanation of unsaturated organic ligands [Equation (1)], would require considerable activation energy to be liberated from its trimer, and thus such direct epitanations [Equation (1)] would understandably be slower than transfer-epitanations [Equation (3)].

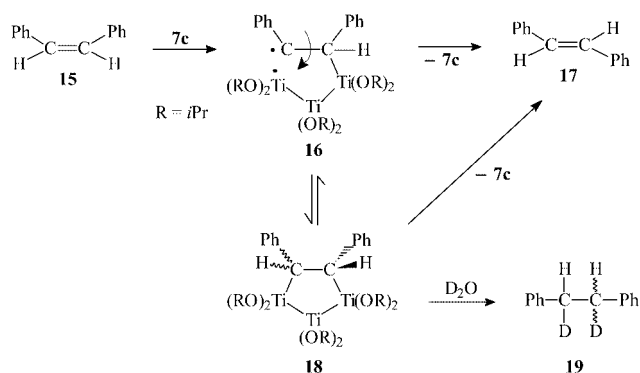
Moreover, certain reactions of $\text{Ti}(\text{OiPr})_2$ (**7**) with organic substrates, as reported in this study, follow pathways consistent with the participation mainly of the trimeric biradical **7c**. For example, with 1 equiv. of diphenylacetylene (**6**) and 2 equiv. of **7**, the addition reaction leading to *cis*-stilbene (**15**) upon hydrolysis proceeded to the extent of 30% at 25 °C. When a similar reaction mixture was heated at reflux, the reaction went only to an extent of 74%, despite the presence of an excess of **7**. Now, if the 2 equiv. of **7** is actually present as trimer **7c**, then the 0.67 equiv. of **7c** could react with only 0.67 equiv. of **6**, close to the observed 0.74 equiv. of **6** consumed. Thus, we conclude that the addition reaction to **6** should be described as involving mostly attack by **7c** [Equation (6)] to form **14**. Hydrolysis would then yield **15** or with D_2O , 1,2-dideuterio-*cis*-stilbene (**9**), as is observed.



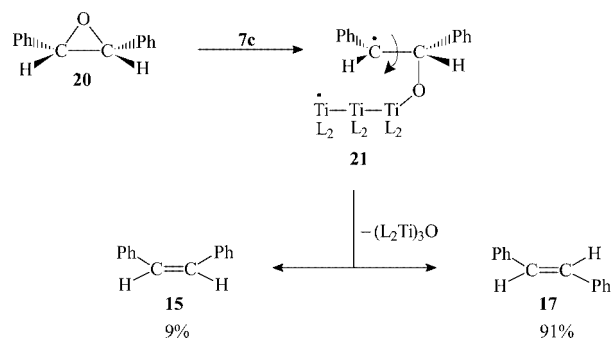
Two other reactions giving evidence for the participation of biradical **7c** directly are those involving *cis*-stilbene (**15**) itself and *cis*-stilbene oxide (**20**). Regardless of how long and at what temperature the reaction proceeded and whether **7** contained LiOiPr or not, the main reaction of a 1:2 equiv. ratio of **15** and **7**, as revealed by hydrolysis, was isomerization to *trans*-stilbene (**17**), rather than addition to form **18** (detected as deuteriolysis product **19**). Workup with D_2O produced 1,2-dideuteriobibenzyl (**19**), consistent with its formation from organotitanium precursor **18**. Again, we suggest that the 0.67 equiv. of trimer **7c** is operative, as shown in Scheme 2. The *trans*-stilbene could be formed directly from **16** by reeliminating **7c** or from **18** by stepwise $\text{Ti}-\text{C}$ bond homolysis. In the conversion of **16** into **17**, the greater thermodynamic stability of **17** over **15** (about 91:9) should favor the formation of the *trans* isomer.

In a similar manner, the deoxygenation of *cis*-stilbene oxide (**20**) by **7** to give the thermodynamic mixture of *trans*- and *cis*-stilbenes (**17** and **15**) in a 91:9 ratio is consistent with the stepwise attack of biradical **7c** on **20** to form an acyclic biradical intermediate **21**. Biradical **21** could exist sufficiently long to permit rotation about the $\text{C}-\text{C}$ bond before the second $\text{Ti}-\text{C}$ bond undergoes induced homolysis and thereby produces the thermodynamic mixture of **15** and **17** (Scheme 3).

The first indication that the isopropoxy ligand exerts an activating effect on titanium(II), over that observed with the chloro ligand, was the faster direct epimetallating action of the $\text{Ti}(\text{OiPr})_2/2\text{LiOiPr}$ system on diphenylacetylene (**6**) over



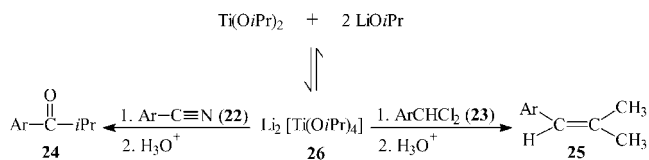
Scheme 2.



Scheme 3.

that of the similar $\text{TiCl}_2/2\text{LiCl}$ reagent (**5**) on **6** [Equation (2) and related text]. The greater reactivity of **7** over **5** has been ascribed to the electron-withdrawal effect of the isopropoxy groups already bonded in **7**, as well as any isopropoxy anions (from the LiOiPr) that may also coordinate with the $\text{Ti}(\text{OiPr})_2$ with the formation of complex titanium(II) anions, such as $[\text{Ti}(\text{OiPr})_4]^{2-}$.^[12]

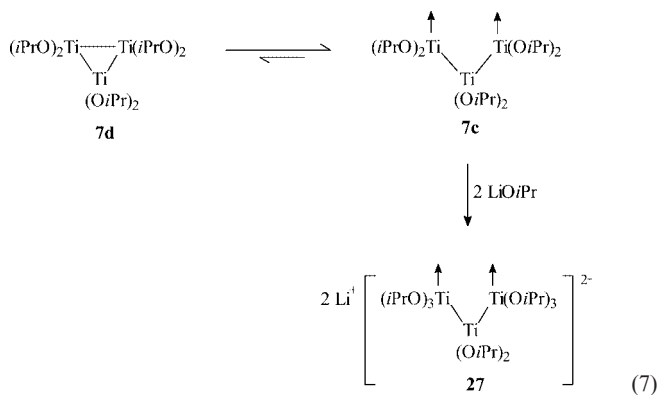
A final previously studied reaction of **7** that clearly involves the participation of radical intermediates in SET (Single Electron Transfer) processes and implicates the by-product LiOiPr as an essential coreactant, is the reaction of **7** with aromatic nitriles (**22**) or geminal dichlorides (**23**), as shown in Scheme 4. The hydrolysis products, **24** and **25** respectively, had individually resulted from a reductive isopropylation. Since $\text{Ti}(\text{OiPr})_2$ containing no LiOiPr byproduct (only LiCl) was unable to bring about such a reaction, the necessary SET reagent was proposed to be **26**, a complex of LiOiPr with the supposed monomer $\text{Ti}(\text{OiPr})_2$.^[12]



Scheme 4.

With the new structural insight into the nature of **7** offered by the present study, we would now propose that trimeric **7c** or **7d** undergoes coordination with one or more equivalents of LiOiPr to form anionic coordination com-

plex(es), such as **27** [Equation (7)]. The coordination of the LiOiPr with adjacent Ti atoms in **7d** or terminal Ti atoms in **7c** would tend to force the Ti trimer into the open-chain dianionic biradical **27**. Therefore, we can deduce from this chemical evidence that a mixture of **7** and LiOiPr most likely exists in solution as one or more coordination complexes of the type depicted in **27**.



A corollary deduction of these considerations is that highly pure titanium(II) diisopropoxide, absolutely free of coordinating anions, such as from LiOiPr or LiCl, and perhaps even free of coordinating solvents such as THF, might well exist at lower temperatures as the diamagnetic trimer **7d**. This possibility is currently under investigation.^[11]

Conclusions

In summary, the EPR experiments show that a Ti-containing molecular triplet state is formed in solution from the reaction of 2 equiv. of butyllithium with 1 equiv. of titanium(IV) isopropoxide. At high concentrations this product, titanium(II) isopropoxide, admixed with 2 equiv. of lithium isopropoxide, is accompanied by the formation of a variety of non-Ti-containing side products. The powder EPR spectrum of the molecular triplet state in frozen solution is consistent with an asymmetric molecule or chain of three Ti centers on which the unpaired electron centers are most probably three centers apart. Dilution experiments show that at lower concentrations, where the non-Ti-containing side products have dissipated, the molecular triplet spectrum intensity varies approximately linearly with concentration. Thus there is no evidence that the observed triplet molecule is one component in a series of concentration-dependent oligomerization steps. Coordination of this open-chain, three-titanium cluster with the lithium isopropoxide byproduct would, for steric reasons, tend to keep such anions in their open-chain biradical form. This steric hindrance for the terminal diisopropoxytitanium centers closing to a ring seems not to be observed with $\text{TiCl}_2 \cdot 2\text{THF}$, which is diamagnetic and may thus exist as an equilateral triangular cluster of three units of $\text{TiCl}_2 \cdot 2\text{THF}$. The smaller steric demand of the chloro and THF units may permit octahedral coordination about each Ti center in such a trigonal array of Ti_3 atoms.

Finally, chemical reactions carried out individually with diphenylacetylene, *cis*-stilbene, or *cis*-stilbene oxide and titanium(II) isopropoxide provide stoichiometric and stereochemical evidence that the attacking titanium(II) reagent is in fact the trimeric biradical **7c**, rather than some monomeric form of titanium(II) isopropoxide. The previously reported SET reductive isopropylation of aromatic nitriles and geminal dichlorides is reinterpreted in light of this new evidence on the structure of titanium(II) isopropoxide, and the essential role of lithium isopropoxide in shaping the detailed structure of the trimeric titanium biradical is explained.

Experimental Section

Starting Materials, Reaction Conditions, and Instrumentation

The starting TiCl_4 and $\text{Ti}(\text{OiPr})_4$ employed were of 98% or greater purity as commercially available, and the *n*-butyllithium used was as a 1.60-M solution in hexane. All reactions, transfers, and separations were carried out under a positive pressure of anhydrous, oxygen-free argon. All solvents, mainly tetrahydrofuran, heptane, and toluene, employed with these air- and moisture-sensitive reagents were dried and distilled from a mixture of sodium metal and benzophenone ketyl prior to use.^[13] The ^1H - and ^{13}C NMR spectra were recorded with a Bruker spectrometer, model EM-360, with tetramethylsilane (Me_4Si) as the internal standard. The chemical shifts reported are expressed on the δ -scale in parts per million (ppm) from the Me_4Si reference signal.

The electron paramagnetic spectra (EPR) measurements were performed with a Bruker EPR spectrometer, model ESP580 X-band, equipped with a split-ring ER4AA9 resonator and were detected with 100-kHz field modulation and phase-sensitive detection. Temperatures below room temperature were achieved with an Oxford Instruments CF935 cryostat and an ITC502 temperature controller. Two types of EPR experiments were performed on solutions of the divalent titanium derivatives in THF, heptane, or 1:1 (v/v) heptane/toluene mixtures: (1) CW EPR scans of various widths (200–1000 Gauss) were performed at room temperature (20–25 °C), mainly about fields corresponding to $g = 2$, and similar CW EPR experiments were performed with solutions flash-frozen at 50 K or 80 K; and then (2) a Hahn-echo detected, pulsed EPR spectrum was acquired at 20 K. Quantitative estimates of the concentrations of paramagnetic components present in the samples were obtained by comparison with the spectrum of a freshly prepared 1.032-mm standard solution of 1,1-diphenyl-2-picrylhydrazyl.

Preparation of Titanium(II) Isopropoxide (7, containing LiOiPr): In a typical procedure on a 10-mmol scale, a solution of titanium(IV) isopropoxide (1.28 g, 10 mmol) in THF (40 mL) and cooled to -78°C was slowly treated with *n*-butyllithium (12.5 mL, 1.6 M) in hexane (20 mmol) in an argon atmosphere. Stirring the light-brown mixture for 2 h at this temperature and then warming to 25 °C over 10 h gave a black, completely soluble mixture of titanium(II) diisopropoxide (**7**) containing lithium isopropoxide (2 equiv.). This THF solution measured directly gave a strong EPR signal (cf. Results) and was employed for reactions with diphenylacetylene (**6**), with *cis*-stilbene (**15**) and with *cis*-stilbene oxide (**20**).^[12]

Upon removal of all volatiles from THF solutions of **7** and redissolving the residue in heptane or 1:1 mixtures of heptane and toluene (v/v), black complete solutions of the 1:2 mixtures of **7** and LiOiPr resulted. For EPR studies, solutions of **7** in a 1:1 heptane/

toluene mixture were prepared individually at concentrations of 20.0, 7.0, 2.0, and 0.7 mM. That the THF had been completely removed was indicated by ^1H NMR spectra of these hydrocarbon solutions of **7**, which showed no ^1H triplets of THF at $\delta = 3.72$ and 1.84 ppm. Instead, only broad ^1H signals of the isopropoxy group were evident at around 4.0 and 1.2 ppm. These hydrocarbon solutions also displayed strong EPR signals.

Preparation of Titanium(II) Diisopropoxide (7**, free of LiOiPr):** To a stirred solution of titanium(IV) chloride (1.89 g, 10 mmol) in THF (40 mL), prepared and maintained under an argon atmosphere at -78°C , in order to avoid cleavage of the THF ring by the TiCl_4 , was added slowly with stirring $n\text{BuLi}$ (2 equiv.) in hexane (12.5 mL, 1.6 M, 20 mmol), and the resulting mixture was stirred for 30 min. The di-*n*-butyltitanium(IV) dichloride thereby formed was then treated with isopropyl alcohol (2 equiv., 1.20 g, 20 mmol), also at -78°C . The resulting mixture was warmed to 25°C over 10 h, and the dark brown suspension of the proposed titanium(IV) dichloride diisopropoxide was cooled again to -78°C . Finally, a further aliquot of $n\text{BuLi}$ (2 equiv.) was added. A subsequent warming of this last reaction product gave a black solution of titanium(II) diisopropoxide from which the white LiCl slowly precipitated. Concentration and cooling of the solution permitted about 1.6 g (94%) of the LiCl to be removed. Thus the yield of titanium(II) seems to have been almost quantitative.^[12]

The careful examination of such titanium(II) diisopropoxide solutions, which contain little LiOiPr or LiCl, will have to await further refinements in mixing the reactants and filtering the solutions to remove suspected paramagnetic particles in suspension. It will be of great interest to learn whether solutions of absolutely pure titanium(II) diisopropoxide show any EPR activity. Such information will be valuable in determining what the role of LiOiPr in influencing the triplet character of trimeric clusters of $[\text{Ti}(\text{OiPr})_2]_3$, commingled with LiOiPr.

Preparation of Titanium(II) Chloride (5**):** In a procedure analogous to the foregoing, a stirred solution of titanium(IV) chloride (1.89 g, 10 mmol) in THF (40 mL) was treated at -78°C under argon with *n*-butyllithium (20 mmol) in hexane. Further stirring at -78°C and warming to 25°C yielded a gray-black suspension of titanium(II) chloride (**5**) and lithium chloride as a 1:2 mixture. The resulting black solution of **5** with suspended LiCl showed no EPR signal, either at 25°C or at lower temperatures.

As already has been published,^[14] titanium(II) chloride (**5**) can be isolated free of LiCl from the suspension in THF by removing the THF and all volatiles under reduced pressure in argon. The residue is then slurried with toluene, and the suspension is filtered to remove all the LiCl. The filtrate is concentrated and chilled, in order to deposit black crystals, whose analysis corresponds to a 1:2 ratio of Ti/Cl and a Ti analysis agreeing with the empirical formula of $\text{TiCl}_2 \cdot \text{THF}$ (**5**). Solutions of **5** in toluene again showed no EPR signal either at room temperature or at 80 K.

Reactions of Titanium(II) Isopropoxide with *cis*-Stilbene (**15**)

(1) The reaction of **15** (5.0 mmol, 0.89 mL) with **7** (10 mmol, containing LiOiPr) in THF (30 mL) for 24 h gave a product (880 mg) after hydrolytic workup with aqueous HCl (6 N) and extraction of the organic products into ethyl ether, drying of the ether with Na_2SO_4 , and removal of volatiles by rotary evaporation. Analysis of the product by ^1H NMR spectroscopy showed the presence of 35% of *trans*-stilbene (**17**), 25% of bibenzyl, and 40% of the starting **15**.

(2) A reaction identical to that given above, except that **7** did not contain any LiOiPr, produced a somewhat greater amount of isom-

erization of *cis*-stilbene: 50% of *trans*-stilbene (**17**), 15% of bibenzyl, and 35% of the starting **15**.

(3) A reaction identical to run (1), except that a 3-h reflux period was included, yielded 64% of *trans*-stilbene (**17**), 27% of bibenzyl, and 9% of the starting **15**.

(4) One-half of the reaction mixture in run (3) was worked up with D_2O (min. 98%). The *cis*- and *trans*-stilbenes were found to contain no deuterium, but the bibenzyl was found to be 1,2-dideuteriated (PhCHD-CHDPh , **19**).

Diphenylacetylene (**6**)

(1) A solution of **6** (5.0 mmol, 890 mg) and **7** (10 mmol, containing LiOiPr) in THF (40 mL) was heated at reflux for 12 h and then subjected to the usual hydrolytic workup. Flash column chromatography of the product by using a 60:1 (v/v) hexane/THF mixture showed the presence of 74% of *cis*-stilbene (**15**), 5% of bibenzyl, 1% of hexaphenylbenzene, and 20% of the starting **6**.

(2) A reaction mixture identical with the foregoing was stirred for 24 h at 25°C . Hydrolysis and a similar ^1H NMR analysis revealed the presence of only 30% of *cis*-stilbene (**15**) and 5% of bibenzyl, the rest being unreacted **6**. A deuteriolytic workup produced exclusively *cis*-1,2-dideuterio-*cis*-stilbene (**9**, with deuterons at the vinyl carbons).

(3) A reaction mixture treated as in run (2), except that **7** did not contain any LiOiPr, gave again 31% of **15** and 4% of bibenzyl, essentially in the same product ratio as in section (2).

***cis*-Stilbene Oxide (**20**):** A mixture of **20** (5.0 mmol) and **7** (10 mmol) in THF (30 mL) was allowed to react for 12 h at 25°C . Hydrolytic workup and ^1H NMR analysis of the flash-chromatography eluate obtained with a 60:1 (v/v) mixture of hexane/THF showed the presence of 91% of *trans*-stilbene (**17**) and 9% of its *cis* isomer (**15**).

Acknowledgments

The authors are grateful to the Boulder Scientific Company, Mead, Colorado, for the general support of their research with transition-metal alkyls and to the Alexander von Humboldt Foundation for a Senior Scientist Award to the first-cited author, renewed in 2005 for studies in the laboratory of Professor W. A. Herrmann, Institute of Inorganic Chemistry, Technische Universität München, Munich, Germany.

Furthermore, they thank the Regional Facility for Pulsed EPR and Photochemistry at Binghamton University, established with National Science Foundation support (CHE9512274), for its services in performing the EPR experiments.

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Received: December 1, 2005
Published Online: March 20, 2006