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Notes

Ancillary Ligand Control of the Regiochemistry of Coupling of 3,3-Dimethyl-1-butyne at Titanium Metal Centers

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*Summary: The ambient-temperature sodium amalgam (2 Na per Ti) reduction of hydrocarbon solutions of [Cp(ArO)TiCl$_2$] (ArO = 2,3,5,6-tetraphenylphenoxide) (**1**) in the presence of 3,3-dimethyl-1-butyne yields the 2,5-di(tert-butyl)titanacyclopentadiene compound [Cp(ArO)Ti(C$_4$H$_2$Bu$^t_2$ -2,5)] (**2**). An X-ray diffraction study of **2** confirms the regiochemistry and shows carbon−carbon distances of 1.343(3) and 1.492(3) Å for the double and single bonds, respectively. In contrast the analogous reaction of either [Cp$_2$TiCl$_2$] or [(ArO)$_2$TiCl$_2$] in the presence of 3,3-dimethyl-1-butyne yields the corresponding 2,4-di(tert-butyl)titanacyclopentadiene compounds. When **2** is heated at 100 °C for a few days in C$_6$D$_6$ solution, isomerization to the more stable 2,4-di(tert-butyl) regioisomer **3** is observed by NMR. An attempt is made to rationalize the regiochemistry of the kinetically formed titanacyclopentadiene in terms of steric factors within the intermediate bis(alkyne) complex.*

Introduction

Titanocene dichloride, [Cp$_2$TiCl$_2$], first synthesized by Wilkinson and co-workers,[1] has proven to be a valuable stoichiometric reagent and catalyst precursor in organometallic chemistry. Past research in our group has focused on the use of the bis(aryloxide) compounds [(ArO)$_2$TiCl$_2$], in which the [(ArO)$_2$Ti] unit has an isolobal relationship to the [Cp$_2$Ti] fragment,[2] for carrying out both novel and complementary organic transformations.[3] More recently we have begun to explore the chemistry and synthetic utility of “hybrid” [Cp(ArO)TiCl$_2$] systems containing a variety of chiral and achiral aryloxide ligands.[4] In this note we wish to report on the dramatic difference in regiochemistry of the coupling of *tert*-butyl acetylene by the mixed Cp/OAr system compared to the titanocene and bis(aryloxide) systems.

Results and Discussion

The 2,3,5,6-tetraphenylphenoxide compound [CpTi(OC$_6$HPh$_4$-2,3,5,6)Cl$_2$] (**1**) can be readily obtained in high yield by the addition of 1 equiv of the parent phenol to a mixture of [CpTiCl$_3$] and pyridine in benzene.[4c] The one-electron reduction of related aryloxide compounds has been shown to lead to dinuclear species [Cp(ArO)Ti(μ-Cl)$_2$Ti(OAr)Cp]. When a benzene solution of **1** is reduced by sodium amalgam (2 Na per Ti) in the presence of excess 3,3-dimethyl-1-butyne, formation of the titanacyclopentadiene compound [Cp(ArO)Ti(C$_4$H$_2$Bu$^t_2$-2,5)] (**2**) (ArO = OC$_6$HPh$_4$-2,3,5,6) (Scheme 1) takes place. Analysis by ^{1}H NMR of the crude reaction mixture from the reduction shows no evidence for the presence of the corresponding 2,4-regioisomer (see below). An X-ray diffraction study of **2** confirmed the formulation (Figure 1, Table 1).

In the ^{1}H NMR spectrum of **2**, a sharp Cp resonance is observed at δ 6.56 ppm along with a single Bu^t resonance at δ 1.01 ppm. When a C$_6$D$_6$ solution of **2** is heated at 100 °C in a sealed tube, these resonances slowly drop in intensity with the corresponding buildup of peaks due to a new organometallic product **3**. Compound **3** is characterized by a Cp resonance at δ 5.78 ppm and two new, equal intensity Bu^t resonances at δ 0.93 ppm and 0.82 ppm. The spectroscopic data for **3** are entirely consistent with the 2,4-regioisomer [Cp(ArO)Ti(C$_4$H$_2$Bu$^t_2$-2,4)] (Scheme 1). There is precedence for exactly this type of behavior in the work of Wigley et al.[5] The kinetically formed tantalacyclopentadiene [(ArO)$_2$(Cl)Ta(C$_4$H$_2$Bu$^t_2$-2,5)] (ArO = OC$_6$H$_3$Pr$^i_2$-2,6) was shown to cleanly isomerize to the thermodynamically more stable [(ArO)$_2$(Cl)Ta(C$_4$H$_2$Bu$^t_2$-2,4)] upon heating. However, the kinetic formation of **2** (Scheme 1) contrasts dramatically with the previously reported formation of the 2,4-regioisomer [(ArO)$_2$Ti(C$_4$H$_2$Bu$^t_2$-2,4)] (**4**) (ArO = OC$_6$H$_3$Ph$_2$-2,6) by reduction of the 2,6-diphenylphenoxide [Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2$Cl$_2$] in the presence of 3,3-dim-

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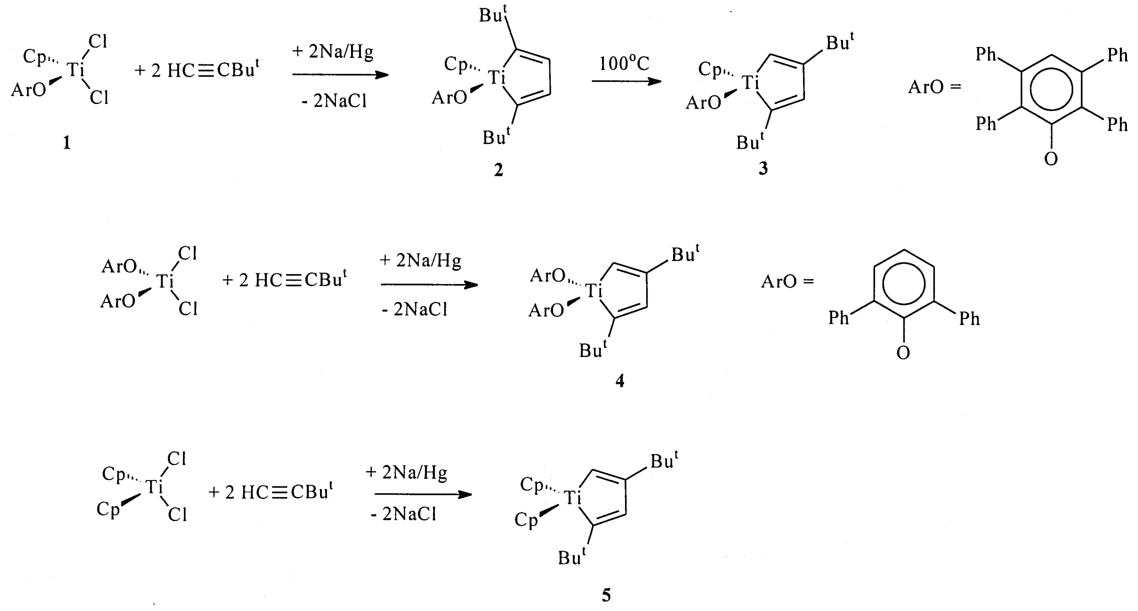
Scheme 1



ethyl-1-butyne (Scheme 1).[3a] We have also shown that use of titanocene dichloride, [Cp_2TiCl_2], as substrate also leads to the 2,4-regioisomer [$Cp_2Ti(C_4H_2Bu^t{}_2\text{-}2,4)$] (**5**) (Scheme 1).

We attempt to rationalize the changes in regiochemistry observed for the kinetically formed titanacyclopentadienes in terms of steric effects within the intermediate bis(alkyne) complexes. The related coupling of two η^2-acyl and/or η^2-iminoacyl groups at group 4 bis(aryloxide) metal centers has been the focus of theoretical investigations.[6] The coupling of two alkyne units at a tungsten bis(aryloxide) metal center to generate a tungstacyclopentatriene ring has also been investigated.[7] In these systems the ground state structure of the precursors does not involve coplanar η^2-acyl, η^2-iminoacyl, or alkyne moieties. Instead, solid and solution ground state structures with parallel units aligned almost along the O−M−O axis are found ([**A**] and [**B**], Scheme 2). In the heteroatom systems in which the units are oriented in a head-to-tail fashion, coupling then occurs by a conrotatory motion, leading to carbon−carbon bond formation. It is interesting that in the actinide-mediated coupling of two acyl units, a ground state coplanar orientation of the two acyl units is followed by a conrotatory acyl motion allowing formation of the final ene-diolate.

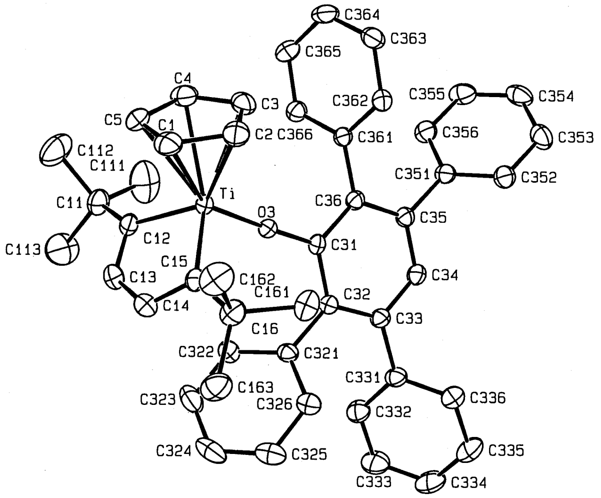


Figure 1. ORTEP (50% thermal ellipsoids) view of [CpTi($OC_6HPh_4\text{-}2,3,5,6$)($C_4H_2Bu^t{}_2\text{-}2,5$)] (**2**).

Table 1. Selected Bond Distances (Å) and Angles (deg) for [CpTi($OC_6HPh_4\text{-}2,3,5,6$)($C_4H_2Bu^t{}_2\text{-}2,5$)] (2)

Ti−O	1.831(1)	Ti−C(12)	2.070(2)
C(12)−C(13)	1.343(3)	C(13)−C(14)	1.492(3)
C(14)−C(15)	1.343(3)	Ti−C(15)	2.067(2)
O−Ti−C(15)	102.94(7)	O−Ti−C(12)	103.91(8)
Ti−C(12)−C(13)	95.0(2)	C(12)−C(13)−C(14)	126.6(2)
C(13)−C(14)−C(15)	126.4(2)	C(14)−C(15)−Ti	95.2(2)
Cp−Ti−O	127.69(9)	Cp−Ti−C(12)	111.41(9)
Cp−Ti−C(15)	109.71(9)	C(12)−Ti−C(15)	96.60(9)

An important question therefore that arises is what is the ground state structure for intermediate bis(alkyne) complexes [(X)(Y)Ti(RCCR′)$_2$] (X, Y = ArO or Cp), and how does this vary with the nature of the ancillary ligands? Recently our group has isolated and structurally characterized “hybrid” bis(iminoacyl) compounds [(ArO)(Cp)Zr(η^2-R′NCR)$_2$].[8] The solid state structure shows a head-to-tail arrangement of iminoacyl units very similar to that found in the bis(aryloxide) derivatives ([**C**], Scheme 2). No corresponding bis(iminoacyl) derivatives of the group 4 metallocenes have been isolated, with ene-diolate formation occurring via a different mechanism.[9] However, a bis(alkyne) adduct of zirconocene has been formed and structurally characterized.[10] In this important case the two alkyne units lie in a coplanar orientation similar to [**D**] in Scheme 2.

For the symmetrical bis(aryloxide) system the most sterically favored situation is one in which C_2 symmetry

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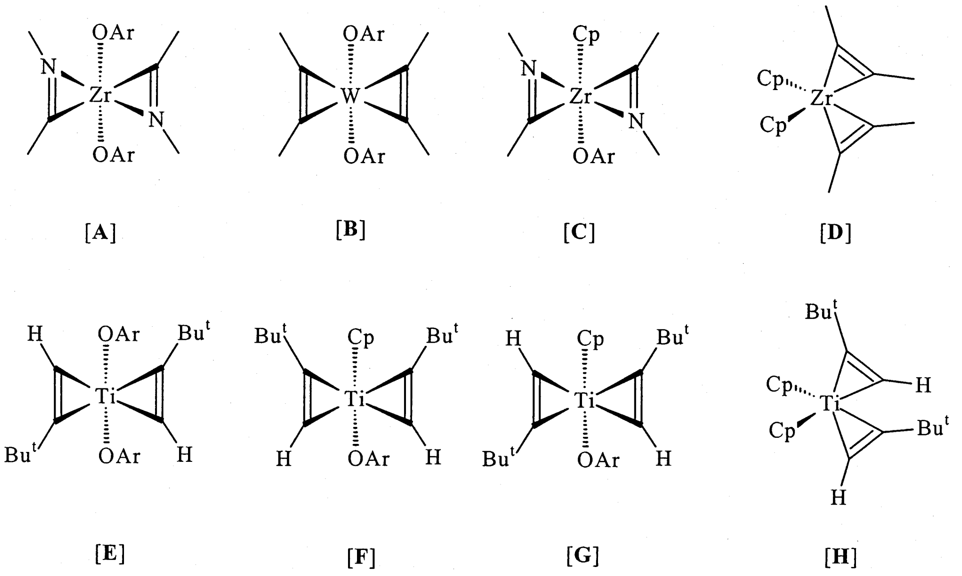
Scheme 2



is present with bulky Bu^t groups away from each other ([**E**], Scheme 2). This then leads to the 2,4-regioisomer upon coupling (the 3,4-isomer being highly unlikely on steric grounds). In the case of the hybrid system, the 2,3,5,6-tetraphenylphenoxide ligand is much bulkier than the Cp unit. Hence a ground state geometry for the bis(alkyne) adduct in which both Bu^t groups are distal to the aryloxide is expected to be favored ([**F**], Scheme 2). This would lead to the observed, 2,5-disubstituted kinetic isomer, which thermally rearranges to the more stable 2,4-regioisomer (Figure 2) in [**G**] in Scheme 2. We presume that the metallocene product arises via in-plane coupling of a bis(alkyne) adduct in which the Bu^t substituents are arranged as shown in [**H**] in Scheme 2.

Experimental Section

General Details. All operations were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. The hydrocarbon solvents were distilled from sodium/benzophenone and stored over sodium ribbons under nitrogen until use. The compound $[CpTi(OC_6HPh_4\text{-}2,3,5,6)Cl_2]$ (**1**) was prepared as previously reported.[4c] The ^1H and ^{13}C NMR spectra were recorded on a Varian Associates Gemini-200, Inova-300, or General Electric QE-300 spectrometer and referenced to protio impurities of commercial benzene-d_6 as internal standard. Elemental analyses and molecular structures were obtained through Purdue in-house facilities.

$[Cp(ArO)Ti(C_4H_2Bu^t{}_2\text{-}2,5)]$ (2) and $[Cp(ArO)Ti(C_4H_2Bu^t{}_2\text{-}2,4)]$ (3) (ArO = OC_6HPh_4-2,3,5,6). A mixture of $[CpTi(OC_6HPh_4\text{-}2,3,5,6)Cl_2]$ (**1**) (1.0 g, 1.72 mmol) and 3,3-dimethyl-1-butyne (1.0 mL, 8.17 mmol) in benzene (25 mL) was stirred above a sodium (0.08 g, 3.48 mmol) amalgam. Over 15 h the color of the mixture changed from orange to greenish brown. The solution was then separated from Hg pool and metal salts by decanting and filtering through a Celite plug and then evacuated to dryness, leaving the crude product as a brown solid. Recrystallization from benzene/hexane yielded the pure compound **2** as orange chunks containing one benzene solvate molecule per Ti. Yield = 0.29 g (26%). Anal. Calcd for $C_{53}H_{52}OTi$; **2**$\cdot C_6H_6$: C, 84.55; H, 6.96. Found: C, 84.15; H, 6.86. ^1H NMR (C_6D_6, 30 °C): δ 7.38−6.92 (aromatics); 6.56 (s, $C_4Bu^t{}_2H_2$); 5.64 (s, C_5H_5); 1.01 (s, CMe_3). ^{13}C NMR (C_6D_6, 30 °C): δ 221.9 ($TiCBu^t$); 110.7 (C_5H_5); 40.8 (CMe_3); 31.1 (CMe_3).

A sample of **2** was dissolved in C_6D_6 in a J. Young valve NMR tube. Over the course of a few days the sample slowly converted to the 2,4-isomer **3** at 100 °C as monitored by NMR. During the course of the isomerization, other products were also formed in solution and a pure sample of **3** was not isolated. ^1H NMR (C_6D_6, 30 °C): δ 7.38−6.92 (aromatics); 6.61 (d, $C_4Bu^t{}_2H_2$, ^4J = 4.5 Hz); 5.78 (s, C_5H_5); 0.93 (s), 0.82 (s, CMe_3). ^{13}C NMR (C_6D_6, 30 °C): δ 194.9 ($TiCBu^t$); 181.3 ($TiCH$); 138.7 ($TiCCH$); 131.7 ($TiCCBu^t$); 142.4 ($Ti{-}O{-}C$); 112.3 (C_5H_5); 40.9, 36.4 (CMe_3), 31.4, 28.3 (CMe_3). **$[Cp_2Ti(C_4H_2Bu^t{}_2\text{-}2,4)]$ (5).** A mixture of $[Cp_2TiCl_2]$ (1.0 g, 4.02 mmol) and 3,3-dimethyl-1-butyne (1.5 mL, 12.3 mmol) in benzene (25 mL) was stirred above a sodium (0.19 g, 8.26 mmol) amalgam. Over 15 h the color of the mixture changed from red to green to brown. The solution was then separated from Hg pool and metal salts by decanting and filtering through a Celite plug and then evacuated to dryness, leaving the product as a brown solid. Yield = 0.59 g (43%). Microanalytical data consistently gave low C%. ^1H NMR (C_6D_6, 30 °C), see Supporting Information: δ 5.99 (d), 5.17 (d, $TiC_4Bu^t{}_2H_2$, ^4J = 16.9 Hz); 5.90 (s, C_5H_5);

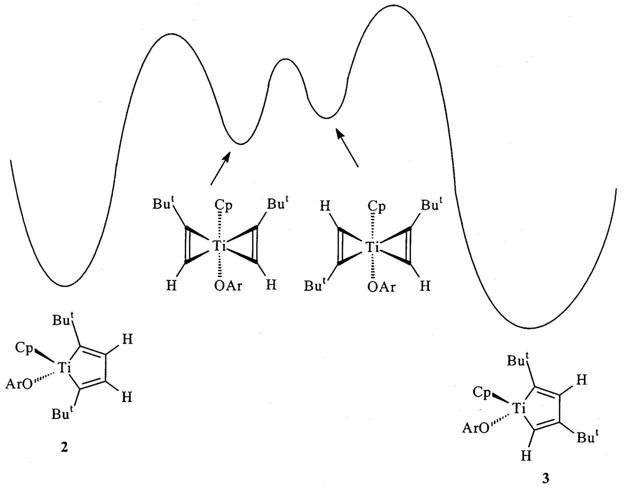


Figure 2. Energy correlation for the conversion of 2,5-disubstituted kinetic isomer **2** to the thermodynamically more stable 2,4-disubstituted isomer **3**.

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Table 2. Crystal Data and Data Collections Parameters for [$CpTi(OC_6HPh_4$-2,3,5,6)($C_4H_2Bu^t{}_2$-2,5)] (2)

	2·C_6H_6
formula	$TiO_1C_{53}H_{52}$
fw	752.90
space group	$P2_1/n$ (No. 14)
a, Å	19.3113(10)
b, Å	10.8549(4)
c, Å	21.2798(8)
α, deg	90
β, deg	108.766(2)
γ, deg	90
V, Å	4223.6(6)
Z	4
ρ_{calc}, g cm^{-3}	1.184
temperature, K	150.
radiation (wavelength)	Mo Kα (0.71073 Å)
R	0.058
R_w	0.129

1.24 (s), 1.00 (s, C*Me*$_3$). ^{13}C NMR (C_6D_6, 30 °C): δ 182.2 (Ti*C*Bu^t); 143.3 (Ti*C*H); 113.4 (*C*$_5$H$_5$); 106.2 (TiC*C*H); 100.2 (TiC*C*Bu^t); 34.8, 31.7 (*C*Me$_3$); 29.9, 28.6(C*Me*$_3$).

X-ray Data Collection and Reduction. A suitable crystal was mounted on a glass fiber in a random orientation under a cold stream of dry nitrogen. Preliminary examination and final data collection were performed with Mo Kα radiation (λ = 0.71073 Å) on a Nonius Kappa CCD. Lorentz and polarization corrections were applied to the data.[11] An empirical absorption correction using SCALEPACK was applied.[12] Intensities of equivalent reflections were averaged. The structure was solved using the structure solution program PATTY in DIRDIF92.[13] The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The structure was refined in full-matrix least-squares where the function minimized was $\sum w(|F_o|^2 - |F_c|^2)^2$ and the weight w is defined as $w = 1/[\sigma^2(F_o{}^2) + (0.0585P)^2 + 1.4064P]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$. Scattering factors were taken from *International Tables for Crystallography*.[14] Refinement was performed on an AlphaServer 2100 using SHELX-97.[15] Crystallographic drawings were done using ORTEP programs.[16]

Acknowledgment. We thank the National Science Foundation (Grant CHE 0078405) for financial support of this research.

Supporting Information Available: ^{1}H NMR (C_6D_6, 30 °C) spectrum of **5**. Tables of thermal parameters, bond distances and angles, intensity data, torsion angles, and multiplicities for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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