New Half-Sandwich Alkyl, Aryl, Aryloxide, and Propargyloxide Titanium(IV) Complexes Containing a Cyclopentadienyl Ligand with a Pendant Ether Substituent: Behavior and Influence in the Hydroamination of Alkynes of the Ether Group

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Received December 2, 2005

The complex Cp^OTiCl_3 (**1**; $Cp^O = C_5H_4CH_2CH_2OCH_3$) reacts with 1.0, 2.0, and 3.0 equiv of MeMgCl to give $Cp^OTiMeCl_2$ (**2**), Cp^OTiMe_2Cl (**3**), and Cp^OTiMe_3 (**4**). In the solid state, the ether group of the pendant substituent of the cyclopentadienyl ligand is coordinated to the metal center (d(Ti−O) = 2.3373(18) Å in **2** and 2.2818(10) Å in **3**) disposed transoid to a methyl ligand. In solution the O-donor substituent is involved in a coordination−dissociation equilibrium ($\Delta H° = 3.0 \pm 0.7$ kcal mol^{-1} and $\Delta S° = 12 \pm 4$ cal mol^{-1} K^{-1} for **2**, $\Delta H° = 4.3 \pm 0.1$ kcal mol^{-1} and $\Delta S° = 17.2 \pm 0.1$ cal mol^{-1} K^{-1} for **3**, and $\Delta H° = 2.3 \pm 0.1$ kcal mol^{-1} and $\Delta S° = 11.9 \pm 0.3$ cal mol^{-1} K^{-1} for **4**). The reactions of **1** with 3.0 equiv of $PhCH_2MgCl$, PhMgCl, and (*p*-tolyl)MgBr lead to Cp^OTiR_3 (R = $PhCH_2$ (**5**), Ph (**6**), *p*-tolyl (**7**)) containing a free pendant ether group. The X-ray structure of **6** shows a β-agostic Ti−H interaction between the metal center and a phenyl group (Ti−C_α−C_β = 139.3(3) and 105.3(2)°). Complex **1** reacts with 1.0 equiv of Li(O-2,6-$^tBu_2$-4-MeC_6H_2) to give the six-coordinate aryloxide derivative Cp^OTi(O-2,6-$^tBu_2$-4-MeC_6H_2)Cl_2 (**8**), which has been also characterized by X-ray diffraction analysis. The structure suggests a significant multiple bond character for the Ti−aryloxide bond (Ti−O−C = 151.31(14)°). The addition of 1.0 and 2.0 equiv of MeMgCl to **8** affords Cp^OTiMe(O-2,6-$^tBu_2$-4-MeC_6H_2)Cl (**9**) and Cp^OTiMe_2(O-2,6-$^tBu_2$-4-MeC_6H_2) (**10**). Treatment of **1** with 1.0, 2.0, and 3.0 equiv of Li(O-2,6-$^iPr_2C_6H_3$) gives rise to Cp^OTi(O-2,6-$^iPr_2C_6H_3$)Cl_2 (**11**), Cp^OTi(O-2,6-$^iPr_2C_6H_3$)$_2$Cl (**12**), and Cp^OTi(O-2,6-$^iPr_2C_6H_3$)$_3$ (**13**). Complex **11** reacts with 1.0 and 2.0 equiv of MeMgCl to afford Cp^OTiMe(O-2,6-$^iPr_2C_6H_3$)Cl (**14**) and Cp^OTiMe_2(O-2,6-$^iPr_2C_6H_3$) (**15**), whereas the reaction of **12** with 1.0 equiv of MeMgCl leads to Cp^OTiMe(O-2,6-$^iPr_2C_6H_3$)$_2$ (**16**). Complexes **15** and **16** can be also obtained by addition of 1.0 and 2.0 equiv of 2,6-diisopropylphenol to **4**. Treatment of **4** with 1.0 and 2.0 equiv of 1,1-diphenyl-2-propyn-1-ol gives the propargyloxide derivatives Cp^OTiMe_2(OCPh$_2$C≡CH) (**17**) and Cp^OTiMe(OCPh$_2$C≡CH)$_2$ (**18**). Like **5**−**7**, complexes **8**−**18** contain a free pendant ether group. Complex **4** is a more efficient catalyst precursor than the related $CpTiMe_3$ (**19**) for the regioselective anti-Markovnikov hydroamination of phenylacetylene with cyclohexylamine, 2,6-dimethylaniline, *tert*-butylamine, and 2,6-diisopropylaniline and for the hydroamination of 1-phenylpropyne and diphenylacetylene with cyclohexylamine and 2,6-dimethylaniline.

Introduction

The subject of titanocenes, their synthesis, structural characterization, and applications to catalysis, has been a very active research area during the last two decades.[1] In recent years, however, a growing interest in monocyclopentadienyltitanium complexes has been evident.[2] This is in part due to the fact that the most active transition-metal catalysts are those containing the lowest number of valence electrons.[3] Within the half-sandwich titanium chemistry, complexes with constrained geometry have been receiving special attention as a consequence of their unique polymerization properties.[4]

A variety of systems based upon alkoxide or aryloxide ligands have been also examined.[5] Reactions that form new carbon−carbon bonds from organic unsaturated compounds such as alkynes and olefins have advanced by the application of titanium alkoxide complexes.[6] In addition, half-sandwich O-2,6-$^iPr_2C_6H_3$ species have shown an exceptionally high catalytic activity not only for ethylene polymerization but also for ethylene−α-olefin

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10.1021/om051031b CCC: $33.50
Publication on Web 02/11/2006

copolymerization in the presence of methylaluminoxane (MAO).[7] Furthermore, half-sandwich titanium alkoxide complexes have been used as models and starting points for the synthesis of peripheral metal dendrimers.[8]

In comparison with the systems with constrained geometry, complexes containing a cyclopentadienyl ligand with a two-electron-donor pendant group remain an underrepresented area within the half-sandwich group 4 metal complexes.[9] Due to the reversible coordination of the pendant group, these types of ligands stabilize highly reactive electrophilic centers until the substrates coordinate and replace the pendant group. The stabilizing effect has a strong influence on the catalytic properties of the active systems.[10] For instance, the complex Cp^NTiCl_3 ($Cp^N = C_5H_4CH_2CH_2NMe_2$)[11] is an active precursor in Ziegler−Natta polymerization catalysis.[12] The amino group affects significantly its catalytic reactivity as compared to that of the parent complex $CpTiCl_3$.[13] Thus, the Cp^NTiCl_3−MAO system shows a considerably lower activity toward styrene and a significantly higher activity toward ethylene and propylene than $CpTiCl_3$−MAO.

Complexes with an ether pendant group are much more scarce than the related N-functionalized compounds.[9d,14] As far as we know, only a few trichloro derivatives have been reported,[15] and alkyl, aryl, and alkoxide complexes are unknown. In the presence of MAO, some of them exhibit a modest activity for styrene and ethylene polymerizations.[16] The low activity has been attributed to an oxygen−aluminum coordination, which could decrease the ability of MAO to abstract an anionic ligand from titanium, and/or to the increase of steric hindrance around the catalytic center as a result of the coordination of the ether pendant group to titanium.

Although the influence of the pendant groups on the catalytic activity of these systems is evident, studies on their behavior in the solid state and in solution are rare in the chemistry of group 4 metals.[15c,e,17] As a part of our work on transition-metal complexes containing a cyclopentadienyl ligand with a pendant donor group,[18] we have recently reported the preparation of $Cp^NTiMe_xCl_{3-x}$ ($x = 1-3$), $Cp^NTiCl(\mu\text{-}O)_2ClTiCp^N$, and $\{(2,6\text{-}{}^iPr_2C_6H_3)NH\}Cp^NTi\{N(2,6\text{-}{}^iPr_2C_6H_3)\}$ ($Cp^N = C_5H_4CH_2CH_2NMe_2$). In the solid state the aminoalkyl substituent of $Cp^NTiMe_xCl_{3-x}$ is weakly bonded to the metal center, disposed transoid to a methyl ligand. In solution the amine dissociates and an equilibrium between seven-coordinate and six-coordinate species is reached. The molar fraction of dissociated amine increases as the number of methyl ligands at the titanium also increases. The amino groups of the dimer compound show a similar behavior.[19] Previously, van der Zeijden and co-workers had proved that the intramolecular coordination of the ether moiety in $(\eta^5\text{-}C_5H_4CH_2CH_2OR)TiCl_3$ (R = Me, menthyl, fenchyl) is also fluxional. From temperature-dependent NMR data, they calculated that at room temperature in dichloromethane-d_2 about of 30% of the pendant group is coordinated to titanium for R = Me, while this figure is significantly lower for the chiral substituents.[15c] In contrast to these systems, the complex $\{(2,6\text{-}{}^iPr_2C_6H_3)NH\}Cp^NTi\{N(2,6\text{-}{}^iPr_2C_6H_3)\}$ contains a pendant dimethylamino group strongly coordinated to the metal center both in the solid state and in solution.[19] In this paper, we report the preparation of the first titanium alkyl, aryl, aryloxide, and propargyloxide complexes containing a (2-methoxyethyl)cyclopentadienyl ligand and show the behavior of their pendant ether group in the solid state and in solution. Furthermore, as a continuation of our work on the development of effective methods of C−N bond formation,[20] we prove that the complex Cp^OTiMe_3 is a more efficient catalyst precursor than the related compound $CpTiMe_3$ (containing an unsubstituted cyclopentadienyl ligand) for the regioselective anti-Markovnikov hydroamination of some alkynes.

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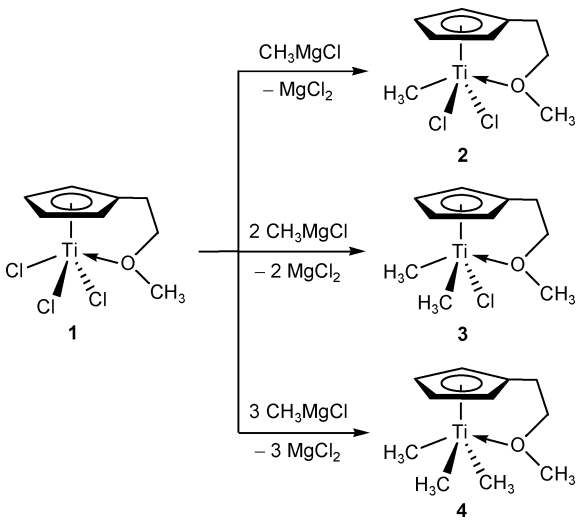
Scheme 1



Results and Discussion

1. Alkyl Derivatives. The addition of 1.0 equiv of MeMgCl in tetrahydrofuran to a suspension of $Cp^{O}TiCl_3$ (**1**) in diethyl ether produces the selective substitution of one of the chloride ligands of **1** by a methyl group and the formation of the monomethyl derivative $Cp^{O}TiMeCl_2$ (**2**), which is isolated as a brown solid in 40% yield, according to Scheme 1.

Figure 1 gives a view of the molecular geometry of **2**, whereas selected bond distances and angles are listed in Table 1. The structure proves the coordination of the ether pendant group to the titanium atom, in the solid state. Thus, the distribution of ligands around the metal center can be described as a four-legged piano-stool geometry, with the cyclopentadienyl ring occupying the three-membered face, while the oxygen atom of the pendant group lies in the four-membered face disposed transoid to the methyl ligand (C(1)−Ti−O = 153.53(9)°). The Ti−O bond length of 2.3373(18) Å is longer than those found in the complexes $\{\eta^5(C_5),\kappa'O\text{-}[C_5H_4CH_2CHCH_2CH_2CH_2O]\}TiCl_3$ (2.165(4) Å),[15a] **1** (about 2.214 Å),[15b] $\{\eta^5(C_5),\kappa'O\text{-}[C_5Me_4CH_2CH_2OCH_3]\}TiCl_3$ (2.295(2) Å),[15e] and $\{\eta^5(C_5),\kappa'O\text{-}[C_5H_4CH(CH_3)CH_2OCH_3]\}TiCl_3$ (2.26(2) and 2.22(3) Å).[15d] However, the Ti−C(1) distance (2.141(3) Å) is statistically identical with the titanium−methyl separations in the complexes $Cp^{N}TiMeCl_2$ (2.144(3) Å) and $Cp^{N}TiMe_2Cl$ (2.150(5) Å trans to N, 2.130(5) Å trans to Cl).[19] The Ti−Cl bond lengths of 2.3114(18) Å (Ti−Cl(1)) and 2.307(2) Å (Ti−Cl(2)) compare well with the related parameters in the aforementioned trichloro derivatives (between 2.29 and 2.32 Å).

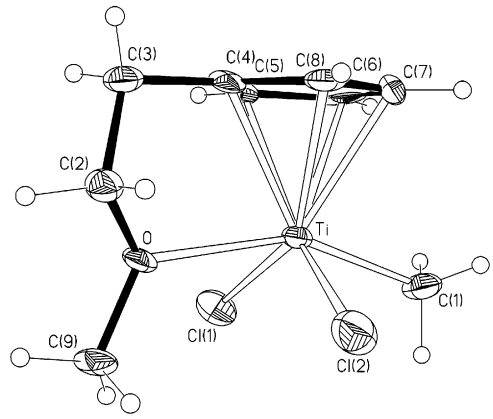


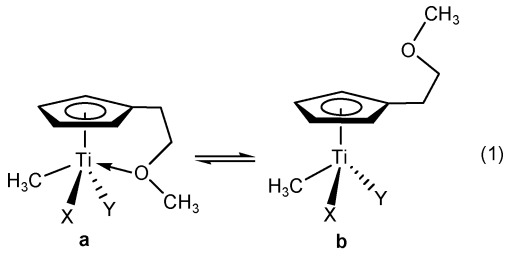
Figure 1. Molecular diagram of $Cp^{O}TiMeCl_2$ (**2**).

Table 1. Selected Bond Distances (Å) and Angles (deg) for the Complex $Cp^{O}TiMeCl_2$ (2)

Ti−Cl(1)	2.3114(18)	Ti−C(7)	2.391(7)
Ti−Cl(2)	2.307(2)	Ti−C(8)	2.373(6)
Ti−C(1)	2.141(3)	C(2)−C(3)	1.561(5)
Ti−O	2.3373(18)	C(3)−C(4)	1.501(3)
Ti−C(4)	2.351(2)	O−C(2)	1.377(5)
Ti−C(5)	2.336(6)	O−C(9)	1.441(3)
Ti−C(6)	2.340(7)		
C(1)−Ti−Cl(1)	88.4(2)	Cl(2)−Ti−M[a]	118.8
C(1)−Ti−Cl(2)	85.2(2)	O−Ti−M	99.9
C(1)−Ti−O	153.53(9)	Ti−O−C(2)	116.8(2)
C(1)−Ti−M	106.5	Ti−O−C(9)	121.53(15)
Cl(1)−Ti−Cl(2)	120.33(3)	C(2)−O−C(9)	114.4(3)
Cl(1)−Ti−O	79.30(15)	O−C(2)−C(3)	106.2(4)
Cl(1)−Ti−M	119.9	C(2)−C(3)−C(4)	109.0(3)
Cl(2)−Ti−O	81.13(16)		

[a] M represents the midpoint of the C(4)−C(8) Cp ligand.

In solution, the pendant O-donor substituent of the cyclopentadienyl ligand is involved in a coordination−dissociation process (eq 1). This is strongly supported by the ^1H and $^{13}C\{^1H\}$ NMR spectra in toluene-d_8, which are temperature dependent. Figure 2 gives the ^1H NMR spectrum as a function of the temperature. At 333 K, the spectrum contains two cyclopentadienyl resonances at 6.09 and 6.02 ppm, two triplets (J_{H-H} = 6.0 Hz) for the pendant chain protons at 3.11 (CH_2O) and 2.38 ppm (CH_2Cp), and singlets at 3.08 (OMe) and 1.75 ppm (TiMe) corresponding to the methyl groups of the molecule. Lowering the sample temperature produces an increase of the separation between the cyclopentadienyl resonances, which at 203 K appear at 6.15 and 5.75 ppm, whereas the triplets due to the pendant chain protons are shifted toward higher field as the temperature decreases. At 203 K, they are observed at 2.48 (CH_2O) and 1.35 ppm (CH_2Cp). On the other hand, both methyl resonances are shifted toward lower field. At 203 K, the OMe singlet appears at 3.26 ppm, whereas the TiMe resonance is observed at 1.94 ppm.



X = Y = Cl (**2**), CH_3 (**4**); X= CH_3, Y= Cl (**3**)

(20) (a) Esteruelas, M. A.; Gómez, A. V.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1996**, *15*, 3423. (b) Albéniz, M. J.; Esteruelas, M. A.; Lledós, A.; Maseras, F.; Oñate, E.; Oro, L. A.; Sola, E.; Zeier, B. *J. Chem. Soc., Dalton Trans*. **1997**, 181. (c) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oñate, E. *Organometallics* **1998**, *17*, 3567. (d) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oñate, E.; Ruiz, N. *Organometallics* **1999**, *18*, 1606. (e) Bernad, D. J.; Esteruelas, M. A.; López, A. M.; Modrego, J.; Puerta, M. C.; Valerga, P. *Organometallics* **1999**, *18*, 4995. (f) Bernad, D. J.; Esteruelas, M. A.; López, A. M.; Oliván, M.; Oñate, E.; Puerta, M. C.; Valerga, P. *Organometallics* **2000**, *19*, 4327. (g) Baya, M.; Crochet, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 240. (h) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 2294. (i) Buil, M. L.; Esteruelas, M. A.; López, A. M.; Oñate, E. *Organometallics* **2003**, *22*, 162. (j) Buil, M. L.; Esteruelas, M. A.; López, A. M.; Oñate, E. *Organometallics* **2003**, *22*, 5274. (k) Asensio, A.; Buil, M. L.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2004**, *23*, 5787. (l) Baya, M.; Esteruelas, M. A.; González, A. I.; López, A. M.; Oñate, E. *Organometallics* **2005**, *24*, 1225. (m) Esteruelas, M. A.; López, A. M. *Organometallics* **2005**, *24*, 3584.

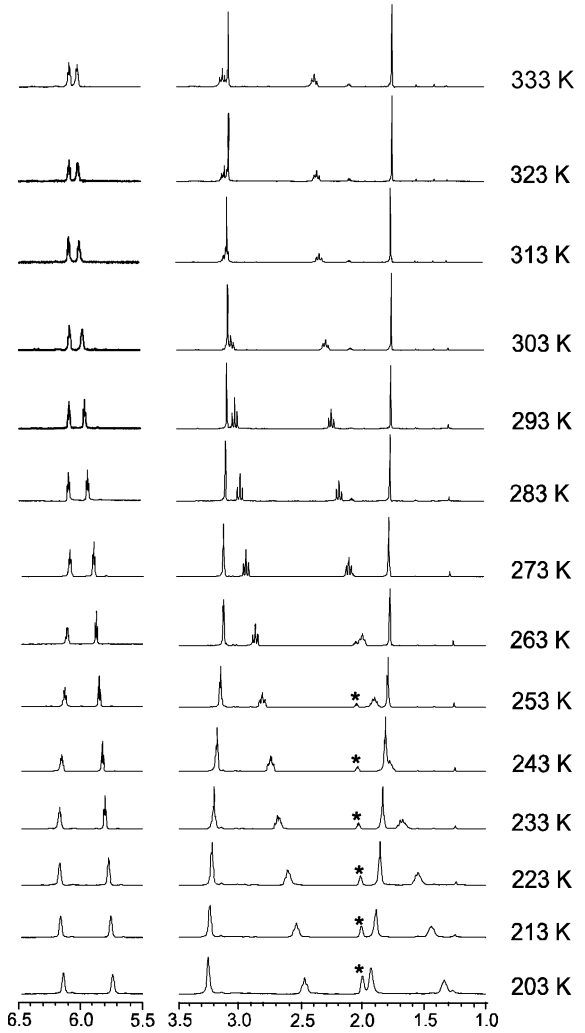


Figure 2. Variable-temperature ^{1}H NMR spectra for complex Cp^O-$TiMeCl_2$ (**2**) (toluene-d_8). Asterisks denote residual solvent peaks.

For the process shown in eq 1, the equilibrium constants between 333 and 203 K were determined according to eq 2.[21]

$$K = \frac{[\mathbf{b}]}{[\mathbf{a}]} = \frac{\delta_{min}(CpCH_2) - \delta(CpCH_2)}{\delta(CpCH_2) - \delta_{max}(CpCH_2)} = \frac{\delta_{min}(CH_2O) - \delta(CH_2O)}{\delta(CH_2O) - \delta_{max}(CH_2O)} \quad (2)$$

The temperature dependence of the equilibrium gives the values $\Delta H° = 3.0 \pm 0.7$ kcal mol^{-1} and $\Delta S° = 12 \pm 4$ cal mol^{-1} K^{-1}. The positive value of $\Delta S°$ is in agreement with the free character of the pendant group in **2b**, whereas the low value of $\Delta H°$ indicates a weak Ti−O bond in **2a**.

Treatment of **1** with 2.0 equiv of MeMgCl produces the substitution of two chloride ligands of the starting compound by methyl groups and the formation of the dimethyl derivative Cp^OTiMe_2Cl (**3**), which is isolated as a red solid in 50% yield (Scheme 1).

Like **2**, complex **3** has been characterized in the solid state by X-ray diffraction analysis. The structure proves that, in this case, the pendant group also coordinates to the titanium atom. Figure 3 gives a view of the molecular geometry. Selected bond distances and angles are collected in Table 2.

(21) Dalling, D. K.; Zilm, K. W.; Grant, D. M.; Heeschen, W. A.; Horton, W. J.; Pugmire, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 4817.

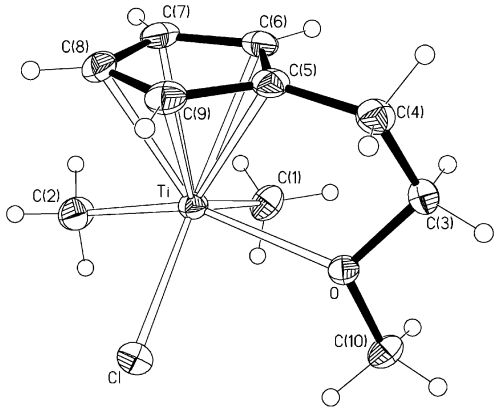


Figure 3. Molecular diagram of Cp^OTiMe_2Cl (**3**).

Table 2. Selected Bond Distances (Å) and Angles (deg) for the Complex Cp^OTiMe_2Cl (3)

Ti−Cl	2.3439(5)	Ti−C(8)	2.3588(16)
Ti−C(1)	2.1344(17)	Ti−C(9)	2.3374(16)
Ti−C(2)	2.1345(17)	O−C(3)	1.4493(18)
Ti−O	2.2818(10)	O−C(10)	1.4395(18)
Ti−C(5)	2.3406(15)	C(5)−C(4)	1.497(2)
Ti−C(6)	2.3659(15)	C(4)−C(3)	1.506(2)
Ti−C(7)	2.3787(15)		
C(1)−Ti−Cl	123.33(5)	C(2)−Ti−M[a]	107.1
C(1)−Ti−C(2)	82.74(8)	O−Ti−M	101.8
C(1)−Ti−O	81.94(6)	Ti−O−C(3)	116.78(9)
C(1)−Ti−M	110.4	Ti−O−C(10)	121.24(9)
Cl−Ti−C(2)	87.99(5)	C(3)−O-C(10)	111.07(12)
Cl−Ti−O	79.65(3)	O−C(3)−C(4)	106.58(13)
Cl−Ti−M	125.6	C(3)−C(4)-C(5)	110.14(13)
C(2)−Ti−O	150.47(6)		

[a] M represents the midpoint of the C(5)−C(9) Cp ligand.

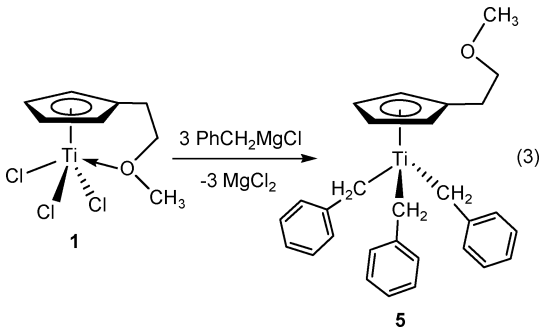
The distribution of ligands around the metal center is similar to that of **2**, with the methyl ligands disposed mutually cisoid (C(1)−Ti−C(2) = 82.74(8)°) and the pendant ether group disposed transoid to C(2) (C(2)−Ti−O = 150.47(6)°). The Ti−C(1) (2.1344(17) Å) and Ti−C(2) distances (2.1345(17) Å) are statistically identical with the related parameter in **2**. However, the Ti−Cl bond length of 2.3439(5) Å is about 0.03 Å longer than the Ti−Cl separations in the latter. On the other hand, the Ti−O distance of 2.2818(10) Å is about 0.05 Å shorter than that in the monomethyl derivative.

In solution, the pendant O-donor substituent of the cyclopentadienyl ligand of **3** is also involved in a coordination−dissociation process like that shown in eq 1. In agreement with this, the behavior of the ^{1}H and ^{13}C{^{1}H} NMR spectra of **3** with the temperature is similar to that described for **2**. In this case, the temperature dependence of the equilibrium gives the values $\Delta H° = 4.3 \pm 0.1$ kcal mol^{-1} and $\Delta S° = 17.2 \pm 0.1$ cal mol^{-1} K^{-1}.

The addition of 3.0 equiv of MeMgCl to a diethyl ether suspension of **1** produces the substitution of the three chloride ligands of the starting complex by methyl groups. As a result, the trimethyl derivative Cp^OTiMe_3 (**4**) is formed, according to Scheme 1. Complex **4** is isolated as an orange oil in 89% yield. In solution, the behavior of the pendant O-donor group of **4** is like that of **2** and **3**. In accordance with this, the ^{1}H and ^{13}C-{^{1}H} NMR spectra of **4** are also temperature dependent and completely analogous to those of **2** and **3**. The values of the parameters $\Delta H°$ and $\Delta S°$, obtained from the temperature dependence of the equilibrium, are 2.3 ± 0.1 kcal mol^{-1} and 11.9 ± 0.3 cal mol^{-1} K^{-1}, respectively.

According to the values of $\Delta H°$ and $\Delta S°$ calculated for **2**−**4,** the molar fraction of hexacoordinate form **b** at 20 °C in toluene-d_8 increases in the sequence **2** (0.71) < **3** (0.78) < **4** (0.88), as

the chloride ligands at the titanium atom are replaced by methyl groups. This appears to be a consequence of the steric hindrance experienced by the ether group and the methyl ligands, when they are disposed mutually cisoid. In agreement with this, the treatment of **1** in diethyl ether with 3.0 equiv of $PhCH_2MgCl$ (bulkier than CH_3) affords the six-coordinate complex $Cp^OTi(CH_2Ph)_3$ (**5**), containing a free ether pendant group, which was isolated as a red oil in 80% yield, according to eq 3.



The free character of the ether substituent of the cyclopentadienyl ligand of **5** in solution is strongly supported by the ^1H and $^{13}C\{^1H\}$ NMR spectra of this compound in toluene-d_8, which, in contrast to those of **2**−**4**, are temperature invariant between 293 and 193 K. The ^1H NMR spectrum shows the phenyl resonances between 7.15 and 6.77 ppm, two cyclopentadienyl signals at 5.66 and 5.49 ppm, two triplets (6.0 Hz) for the pendant chain protons at 3.12 (CH_2O) and 2.14 ppm (CH_2-Cp), and singlets at 3.01 and 2.96 ppm corresponding to the OCH_3 and $TiCH_2$ protons, respectively. In the $^{13}C\{^1H\}$ NMR spectrum, the most noticeable resonance is a singlet at 92.2 ppm due to the TiC carbon atoms.

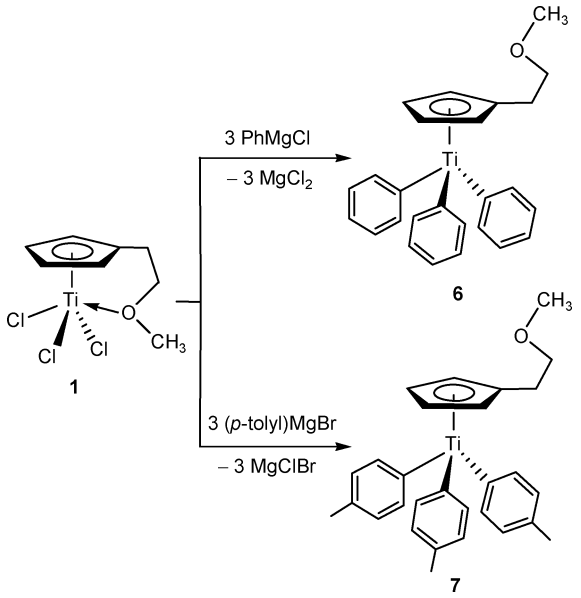
We note that the pentamethylcyclopentadienyl tribenzyl derivative (η^5-C_5Me_5)$Ti(CH_2Ph)_3$ has been previously reported. Its structure, determined by X-ray diffraction analysis, suggests that one of the benzyl groups is involved in an α-agostic Ti···H interaction. However, the ^1H NMR spectrum of the complex, as that of **5**, shows resonances for only one type of benzyl ligand, even at −70 °C.[22]

2. Aryl Derivatives. Complex **1** also reacts with PhMgCl. Its treatment in diethyl ether at −50 °C with 3.0 equiv of the organomagnesium reagent leads to the triaryl derivative Cp^OTiPh_3 (**6**), which is isolated at −78 °C as greenish yellow crystals in 40% yield, according to Scheme 2.

A view of the molecular geometry of **6** is shown in Figure 4. Selected bond distances and angles are listed in Table 3. The structure proves that in the solid state the pendant ether substituent of the cyclopentadienyl ligand is not coordinated to the titanium atom. Thus, the geometry around the metal center can be described as a very distorted octahedron, with the cyclopentadienyl group occupying a face. The distortion is revealed by the C(9)−Ti−C(15) (104.47(13)°), C(9)−Ti−C(21) (108.79(14)°) and C(15)−Ti−C(21) (102.23(13)°) angles, which strongly deviate from the ideal value of 90°.

Without a shadow of a doubt, the most noticeable features of the structure are the parameters related to the C(9)-aryl ligand. The Ti−C(9) bond length of 2.079(3) Å is about 0.04 Å shorter than the Ti−C(21) distance (2.125(3) Å) and about 0.05 Å shorter than the Ti−C(15) separation (2.131(4) Å). Both Ti−C_α−C_β angles for the C(21)- and C(15)-aryl groups show very similar values, between 118 and 124°. However, for the C(9)-aryl ligand, they show a marked difference. While the Ti−C(9)−C(10) angle is 139.3(3)°, the Ti−C(9)−C(14) angle is 105.3(2)°. The shortening of the Ti−C(9) bond length, with regard to the

Scheme 2



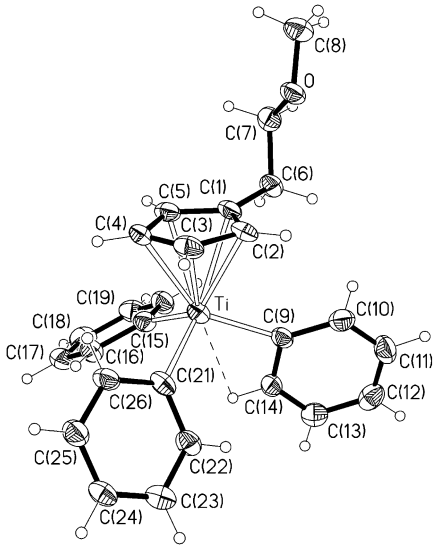


Figure 4. Molecular diagram of Cp^OTiPh_3 (**6**).

Table 3. Selected Bond Distances (Å) and Angles (deg) for the Complex Cp^OTiPh_3 (6)

Ti-C(9)	2.079(3)	C(6)−C(7)	1.515(4)
Ti−C(15)	2.131(4)	O−C(7)	1.411(4)
Ti−C(21)	2.125(3)	O−C(8)	1.408(4)
Ti−C(1)	2.388(3)	Ti−H(14)	2.65
Ti−C(2)	2.372(3)	Ti−H(10)	3.47
Ti−C(3)	2.349(4)	Ti−H(16)	3.14
Ti−C(4)	2.331(3)	Ti−H(20)	3.14
Ti−C(5)	2.356(3)	Ti−H(22)	3.06
C(1)−C(6)	1.515(4)	Ti−H(26)	3.21
C(9)−Ti−C(15)	104.47(13)	C(7)−C(6)−C(1)	111.0(3)
C(9)−Ti−C(21)	108.79(14)	Ti−C(9)−C(10)	139.3(3)
C(9)−Ti−M[a]	114.5	Ti−C(9)−C(14)	105.3(2)
C(15)−Ti−C(21)	102.23(13)	Ti−C(15)−C(16)	121.5(3)
C(15)−Ti−M	112.4	Ti−C(15)−C(20)	122.6(3)
C(21)−Ti−M	113.4	Ti−C(21)−C(22)	118.6(3)
C(8)−O−C(7)	110.9(3)	Ti−C(21)−C(26)	124.3(3)
O−C(7)−C(6)	109.3(3)		

[a] M represents the midpoint of the C(1)−C(5) Cp ligand.

(22) Mena, M.; Pellinghelli, M. A.; Royo, P.; Serrano, R.; Tiripicchio, A. *J. Chem. Soc., Chem. Commun.* **1986**, 1118.

Ti−C(21) and Ti−C(15) distances, and the reduction of the Ti−C(9)−C(14) angle, with regard to the expected value of about 120°, allows the approach of H(14) to the metal atom to establish a β-agostic Ti···H interaction. The Ti−H(14) separation of 2.65 Å compares well with the values reported for other Ti−H agostic interactions.[22,23]

Although the agostic interaction is clearly evident in the crystal structure, no evidence is observed in solution. Thus, in dichloromethane at 183 K, the ^{13}C NMR spectrum shows four aryl resonances at 198.3 (TiC), 132.1 (HC_{meta}), 129.2 (HC_{para}), and 126.1 ppm (HC_{ortho}) with H−C coupling constants of 156 Hz in the three cases. In the ^1H NMR spectrum, the cyclopentadienyl resonances are consistent with the free character of the pendant ether substituent and agree well with those of **5**. The C_5H_4 protons display two signals at 6.76 and 6.58 ppm and the pendant chain protons give rise to triplets (6.0 Hz) at 3.39 (CH_2O) and 2.32 ppm (CH_2Cp), whereas the MeO singlet appears at 3.21 ppm.

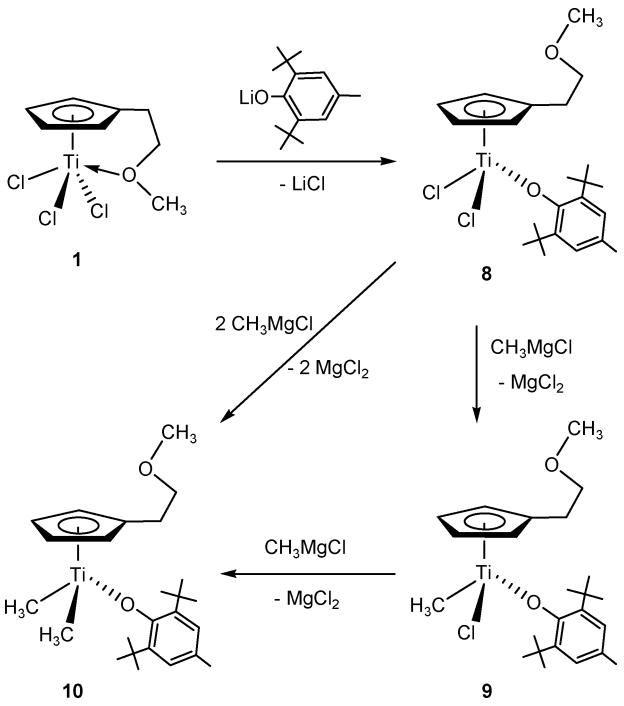
Complex **6** is notable, because is a rare example of a half-sandwich triaryl derivative in the chemistry of the group 4 metals. As far as we know, titanium complexes of this type have not been previously reported. In addition, it should be mentioned that its stability is very low, significantly lower than that of the trialkyl derivatives **4** and **5**. In the solid state and in solution, complex **6** rapidly decomposes to give a complex mixture of unidentified species.

The introduction of a methyl substituent in the phenyl groups, disposed in a para position with regard to the titanium atom, produces a slight increase in the stability of the system. Thus, the treatment of **1** in diethyl ether at −50 °C with 3.0 equiv of (*p*-tolyl)MgBr leads to $Cp^OTi(p\text{-tolyl})_3$ (**7** in Scheme 2), which is isolated as a green oil in 37% yield and, in contrast to **6**, can be characterized at room temperature by ^1H NMR spectroscopy. The spectrum is temperature invariant, agrees well with that of **6**, and supports the free character of the pendant ether group. The C_5H_4 signals appear at 6.74 and 6.59 ppm, the pendant chain protons give rise to triplets (6.0 Hz) at 3.45 (CH_2O) and 2.43 (CH_2Cp) ppm, and the MeO singlet is observed at 3.29 ppm. As in **6**, the $^{13}C\{^1H\}$ NMR spectrum of **7** is temperature invariant and does not show any evidence for a β-agostic Ti−H interaction in solution. Thus, the aryl groups give rise to four resonances, which are observed at 197.8 (TiC_α), 139.1 (CH_3C_δ), 133.5 (C_γ), and 127.5 (C_β) ppm.

3. Aryloxide Derivatives. Treatment of **1** in diethyl ether with 1.0 equiv of Li(O-2,6-^{t}Bu$_2$-4-MeC_6H_2) produces the replacement of one of the chloride ligands of **1** by the aryloxide group to afford Cp^OTi(O-2,6-^{t}Bu$_2$-4-MeC_6H_2)Cl_2 (**8**), which is isolated as a red solid in 76% yield, according to Scheme 3. The use of 2.0 or 3.0 equiv of aryloxide reagent does not give rise to the substitution of more chloride ligands of the starting compound.

Complex **8** has been characterized by X-ray diffraction analysis. Figure 5 shows a view of its molecular geometry, whereas Table 4 collects selected bond distances and angles. In agreement with the request for space of the aryloxide ligand, the structure shows that in the solid state the pendant ether substituent of the cyclopentadienyl ligand is not coordinated to the titanium atom. Thus, the geometry around the metal center can be described as a distorted octahedron, with the cyclopentadienyl group occupying a face and Cl(1)−Ti−Cl(2), Cl(1)−Ti−O(1), and Cl(2)−Ti−O(1) angles of 98.09(3), 104.92(5), and 104.74(5)°, respectively, in the opposite face. The Ti−O(1) bond length of 1.7946(15) Å compares well with those found in other alkoxide compounds,[5,24] and it is consistent with a significant multiple character for the Ti−O bond due to the π-donor power of the oxygen atom.[25] The π-donation from the

Scheme 3



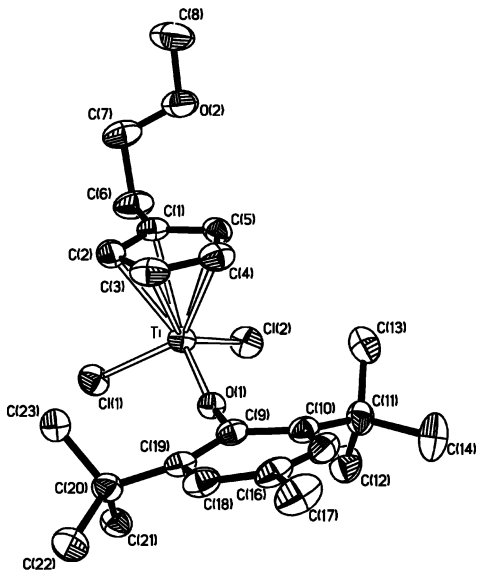


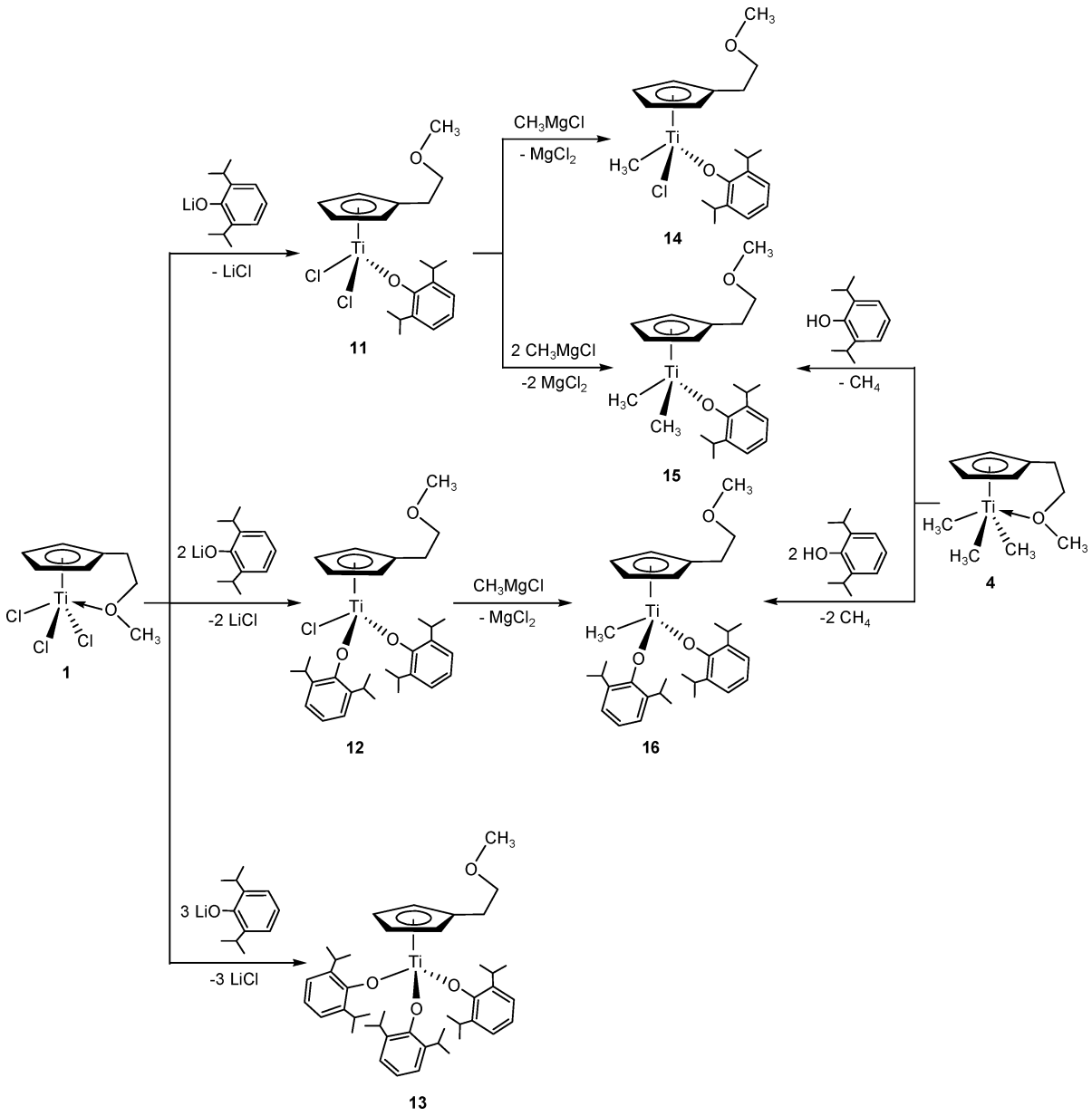
Figure 5. Molecular diagram of Cp^OTi(O-2,6-^{t}Bu$_2$-4-MeC_6H_2)Cl_2 (**8**).

Table 4. Selected Bond Distances (Å) and Angles (deg) for the Complex Cp^OTi(O-2,6-^{t}Bu$_2$-4-MeC_6H_2)Cl_2 (8)

Ti−Cl(1)	2.2546(8)	Ti−C(4)	2.330(2)
Ti−Cl(2)	2.2618(8)	Ti−C(5)	2.335(2)
Ti−O(1)	1.7946(15)	C(1)−C(6)	1.491(3)
O(1)−C(9)	1.378(2)	C(6)−C(7)	1.516(3)
Ti−C(1)	2.354(2)	O(2)−C(7)	1.399(3)
Ti−C(2)	2.347(2)	O(2)−C(8)	1.419(3)
Ti−C(3)	2.331(2)		
Cl(1)−Ti−Cl(2)	98.09(3)	O(1)−Ti−M[a]	117.1
Cl(1)−Ti−O(1)	104.92(5)	C(9)−O(1)−Ti	151.31(14)
Cl(1)−Ti−M	114.7	C(8)−O(2)−C(7)	111.7(2)
Cl(2)−Ti−O(1)	104.74(5)	O(2)−C(7)−C(6)	108.3(2)
Cl(2)−Ti−M	115.1	C(7)−C(6)−C(1)	111.5(2)

[a] M represents the midpoint of the C(1)−C(5) Cp ligand.

Scheme 4



oxygen atom into the titanium is also supported by the Ti−O(1)−C(9) angle of 151.31(14)°, which is certainly greater than that expected from a pyramidal oxygen atom. The Ti−Cl(1) and Ti−Cl(2) distances of 2.2546(8) and 2.2618(8) Å, respectively, are similar to those found in other half-sandwich titanium dichloro aryloxide complexes.[5a,7c] However, they are between 0.05 and 0.06 Å shorter than those of **2** and **3**. The difference seems to be related to the fact that **8** possesses one ligand less than **2** and **3**.

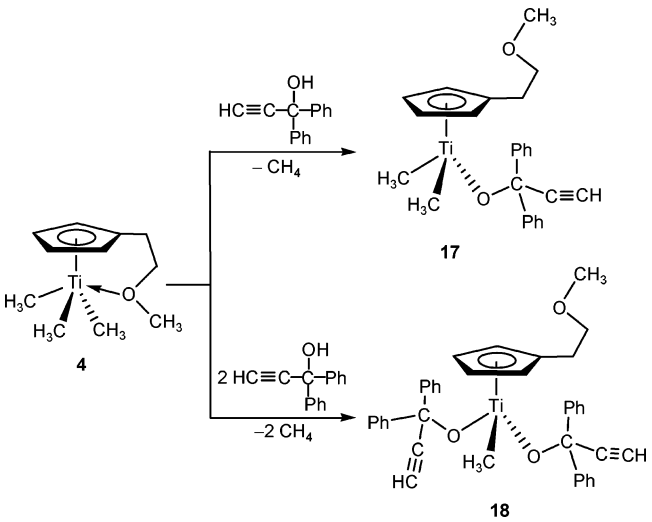
In solution, the pendant ether group is also free. In agreement with this, the ^{1}H and ^{13}C{^{1}H} NMR spectra of **8** are temperature invariant and fully consistent with those of **5**−**7**. The C_5H_4 protons display two signals at 6.32 and 5.91 ppm, whereas the pendant chain protons appear at 3.27 and 2.96 ppm and the MeO singlet is observed at 2.98 ppm.

Complex **8** in diethyl ether reacts with 1.0 equiv of MeMgCl to afford $Cp^OTiMe(O\text{-}2,6\text{-}^tBu_2\text{-}4\text{-}Me\text{-}C_6H_2)Cl$ (**9**), as an orange oil in 69% yield. The reaction of **8** with 2.0 equiv of MeMgCl gives rise to $Cp^OTiMe_2(O\text{-}2,6\text{-}^tBu_2\text{-}4\text{-}MeC_6H_2)$ (**10**), as a yellow oil in 60% yield. Complex **10** can be also obtained by addition of 1.0 equiv of MeMgCl to **9** (Scheme 3). The pendant ether groups of **8** and **9** do not coordinate to the metal center. In accordance with this, the ^{1}H and ^{13}C{^{1}H} NMR spectra are temperature invariant and fully consistent with those of **5**−**8**. The most noticeable spectroscopic feature of these compounds is the presence of four C_5H_4 resonances, at 6.39, 5.90, 5.86, and 5.57 ppm, in the ^{1}H NMR spectrum of **9**. This is a result of the chirality of the metal center.

In contrast to the case for $Li(O\text{-}2,6\text{-}^tBu_2\text{-}4\text{-}MeC_6H_2)$, the addition of 1.0, 2.0, and 3.0 equiv of $Li(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ to **1** in diethyl ether produces the substitution of one, two, and three chloride ligands of the starting compound to afford the aryloxide derivatives $Cp^OTi(O\text{-}2,6\text{-}^iPr_2C_6H_3)Cl_2$ (**11**), $Cp^OTi(O\text{-}2,6\text{-}^iPr_2C_6H_3)_2Cl$ (**12**), and $Cp^OTi(O\text{-}2,6\text{-}^iPr_2C_6H_3)_3$ (**13**), which are isolated as a reddish orange solid in 93% yield, a yellow oil in 45% yield, and an orange oil in 35% yield, respectively, according to Scheme 4. A comparison of the yields of these substitutions clearly indicates that the difficulty of the replacement increases as the number of substituted chloride ligands is augmented: i.e., as the steric hindrance around the metal center grows.

Similarly to **8**, complex **11** reacts with 1.0 and 2.0 equiv of MeMgCl to give $Cp^OTiMe(O\text{-}2,6\text{-}^iPr_2C_6H_3)Cl$ (**14**) and Cp^O-

Scheme 5



$TiMe_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ (**15**), which are isolated as orange and yellow oils in 84% and 98% yields, respectively. The reaction of **12** with 1.0 equiv of MeMgCl leads to $Cp^OTiMe(O\text{-}2,6\text{-}^iPr_2C_6H_3)_2$ (**16**), as an orange oil in 69% yield. Complexes **15** and **16** can be also obtained by treatment of **4** with 1.0 and 2.0 equiv of 2,6-diisopropylphenol, respectively, in diethyl ether at room temperature. The yields of these reactions, 94% for the first of them and 55% for the second one, are consistent with the yields of the reactions of **1** with $Li(O\text{-}2,6\text{-}^iPr_2C_6H_3)$. The addition of 3.0 equiv of 2,6-diisopropylphenol to **4** does not give **13** but **16**.

Complexes **11**−**16** are six-coordinate species with a free pendant ether group. In agreement with this, the ^1H and $^{13}C\{^1H\}$ NMR spectra of these compounds are consistent with those of **5**−**10** and are temperature invariant. The most noticeable spectroscopic features are four C_5H_4 resonances between 6.24 and 5.68 ppm in the ^1H NMR spectrum and between 117.8 and 115.5 ppm in the $^{13}C\{^1H\}$ NMR spectrum of the chiral complex **14**.

4. Propargyloxide Derivatives. Complex **4** also reacts with 1,1-diphenyl-2-propyn-1-ol (Scheme 5). The addition of 1.0 equiv of this alkynol to a tetrahydrofuran solution of **4** produces the release of a methane molecule and the formation of $Cp^O\text{-}TiMe_2(OCPh_2C{\equiv}CH)$ (**17**), which is isolated as a green oil in 94% yield. The reaction of **4** with 2.0 equiv of alkynol leads to $Cp^OTiMe(OCPh_2C{\equiv}CH)_2$ (**18**), as a light yellow solid in 42% yield. The formation of a tripropargyloxide species by addition of 3.0 equiv of 1,1-diphenyl-2-propyn-1-ol to **4** is not observed.

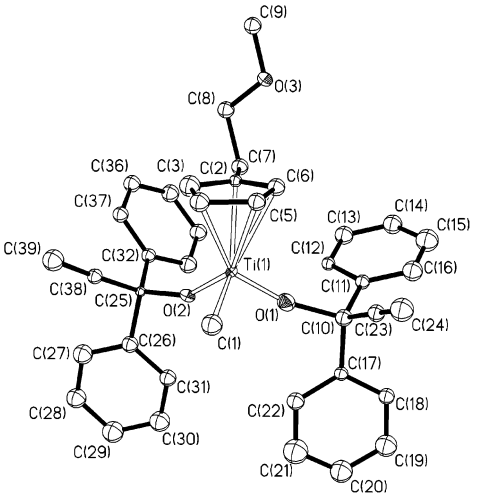


Figure 6. Molecular diagram of $Cp^OTiMe(OCPh_2C{\equiv}CH)_2$ (**18**).

The alkynol 1,1-diphenyl-2-propyn-1-ol contains two relatively acidic protons, the H−C(sp) and H−OC hydrogen atoms. Thus, at first glance, the reactions with **4** could afford **17** and **18** or alternatively alkynyl derivatives. Titanium−alkynyl complexes are known,[26] and the formation of alkynyl derivatives by protonation of Brönsted bases with terminal alkynes, including alkynols, is a broadly studied process in late-transition-metal chemistry.[27] The obtained products from the reactions of **4** with 1,1-diphenyl-2-propyn-1-ol is a new, very nice illustration of the differences in behavior between early and late transition metals. The formation of **17** and **18** instead of alkynyl species is a consequence of the greater energy of the Ti−O bond with regard to the Ti−C bond.[28]

Complexes **17** and **18,** like **11**−**16,** are six-coordinate species, with a free pendant ether group, and display ^1H and $^{13}C\{^1H\}$ NMR spectra consistent with those of **5**−**16**. In the ^1H NMR spectra the most noticeable resonance is a singlet at 2.31 (**17**) or 2.36 ppm (**18**), corresponding to the HC(sp) proton of the propargyloxide ligands. In the $^{13}C\{^1H\}$ NMR spectra the resonances due to the C(sp) atoms appear at about 86 (C) and 75 ppm (CH).

Complex **18** was further characterized by an X-ray crystallographic study. Although a discussion of the structural parameters is not possible because of low precision of the crystallographic data (R1 = 0.23), the structure (Figure 6) proves the free character of the pendant ether group and the coordination of the oxygen atom instead of the terminal C(sp) atom of the monodentate unsaturated ligand.

5. Hydroamination of Alkynes Catalyzed by 4. The direct addition of a N−H bond across a carbon−carbon triple bond constitutes an atom-economical method for the synthesis of nitrogen-containing molecules from inexpensive starting materials.[29] In this context, it should be pointed out that complex **4** is a very efficient catalyst precursor for the regioselective anti-Markovnikov hydroamination of phenylacetylene and 1-phenylpropyne and the hydroamination of diphenylacetylene with amines such as cyclohexylamine, 2,6-dimethylaniline, *tert*-

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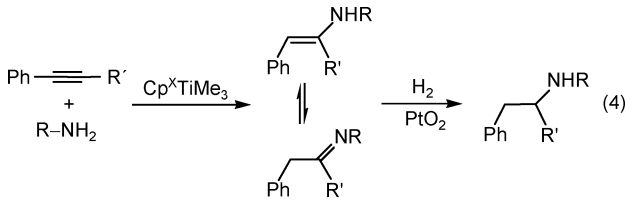
butylamine, and 2,6-diisopropylaniline. Complex **4** is significantly more efficient than the related N-functionalized compound $Cp^{N}TiMe_3$.[19] The reactions were performed in toluene at 100 °C using 5 mol % of catalyst precursor. Under these conditions the alkynes react with the amines to afford the corresponding enamine−imine mixtures, which were transformed in quantitative yield into the secondary amines by reduction with molecular hydrogen in the presence of PtO_2 (eq 4).



(4)

R = Cy, 2,6-$Me_2C_6H_3$, *tert*-butyl, 2,6-$^{i}Pr_2C_6H_3$;
R´ = H, Me, Ph; Cp^{X} = Cp^{O}, Cp

The pendant ether group certainly has a marked influence in the reactivity of **4**. This is clearly evident when the results of the hydroamination in the presence of **4** are compared with those in the presence of the parent complex $CpTiMe_3$ (**19**), which contains an unsubstituted cyclopentadienyl ligand (Table 5).

The hydroamination products from phenylacetylene are obtained in high yield within a short time (0.16−8 h) and with extremely high regioselectivity. Thus, pleasingly, the anti-Markovnikov products are exclusively formed in all the cases. The difference in efficiency between **4** and **19** is particularly noteworthy in the reaction with 2,6-dimethylaniline (entries 3 and 4). Using complex **4** as catalyst precursor, 100% conversion is reached after 2.5 h, while in the presence of **19** only 73% of the alkyne is converted into hydroamination products after 8 h. The catalyst precursor has also a marked influence on the resulting molar ratio of enamine to imine. This is clearly shown in the reactions with 2,6-diisopropylaniline (entries 7 and 8). In the presence of **4**, the enamine is the main hydroamination product (73:27). However, the imine is the major derivative obtained with **19** (15:85).

The replacement of the H−C(sp) hydrogen atom in the alkyne by a methyl group facilitates the hydroamination of the carbon−carbon triple bond, without affecting the regioselectivity of the process. The reactions with 1-phenylpropyne are easier than those with phenylacetylene, not only in the presence of **4** but also with **19**. Complex **4** is more efficient than **19** in reactions involving sterically less demanding amines such as cyclohexylamine (entries 9 and 10) and 2,6-dimethylaniline (entries 11 and 12). For the latter, complex **4** is even more efficient than the bis(indenyl) derivative Ind_2TiMe_2, which has been regarded a "general catalyst".[30] In the hydroamination with bulky amines, the pendant ether group of the cyclopentadienyl ligand of **4** and the substituents at the carbon−carbon triple bond of the internal alkyne appear to experience a large steric hindrance. In accordance with this, complex **19** is a more efficient catalyst

Table 5. Hydroamination of Alkynes Using 4 and 19 as Catalysts[a]

Entry	Catalyst	Alkyne	Amine	*t* (h)	Conv. (%)[b]	Enamine : imine[c]
1	**4**	Ph—≡—H		8	68	32 : 68
2	**19**	Ph—≡—H		8	40	47 : 53
3	**4**	Ph—≡—H		2.5	100	65 : 35
4	**19**	Ph—≡—H		8	73	49 : 51
5	**4**	Ph—≡—H		0.16	100	47 : 53
6	**19**	Ph—≡—H		0.16	100	55 : 45
7	**4**	Ph—≡—H		3.5	100	73 : 27
8	**19**	Ph—≡—H		4	100	15 : 85
9	**4**	Ph—≡—Me		0.83	100	18 : 82
10	**19**	Ph—≡—Me		8	37	18 : 82
11	**4**	Ph—≡—Me		0.5	100	12 : 88
12	**19**	Ph—≡—Me		1	100	10 : 90
13	**4**	Ph—≡—Me		0.75	100	88 : 12
14	**19**	Ph—≡—Me		0.25	100	40 : 60
15	**4**	Ph—≡—Me		2	100	76 : 24
16	**19**	Ph—≡—Me		0.16	100	0 : 100
17	**4**	Ph—≡—Ph		1	100	43 : 57
18	**19**	Ph—≡—Ph		8	92.5	56 : 44
19	**4**	Ph—≡—Ph		1	95	75 : 25
20	**19**	Ph—≡—Ph		2	100	28 : 72
21	**4**	Ph—≡—Ph		3.5	98	100 : 0
22	**19**	Ph—≡—Ph		2	100	100 : 0
23	**4**	Ph—≡—Ph		8	60	90 : 10
24	**19**	Ph—≡—Ph		0.5	100	100 : 0

[a] Reaction conditions: alkyne (2.40 mmol), amine (2.64 mmol), *n*-octane (2.40 mmol), catalyst (0.12 mmol, 5 mol %), toluene (2.0 mL), 100 °C. [b] Determined by GC. [c] Determined by ^{1}H NMR spectroscopy at the end of the reaction.

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precursor than **4** for the reactions involving *tert*-butylamine and 2,6-diisopropylaniline.

Despite the steric hindrance experienced between the pendant ether group of the cyclopentadienyl ligand and the substituents of the alkynes, complex **4** is also a very efficient catalyst precursor for the hydroamination of diphenylacetylene, which contains a sterically more demanding substituent at the carbon−carbon triple bond than the methyl group. Thus, in this case again, the hydroamination products are obtained in high yields (60−100%) within a short time (1−8 h). As for the hydroamination of 1-phenylpropyne, for the reactions with cyclohexylamine (entries 17 and 18) and 2,6-dimethylaniline (entries 19 and 20) complex **4** is more efficient than **19**. However, the latter is more efficient than **4** for the reactions involving *tert*-butylamine (entries 21 and 22) and 2,6-diisopropylaniline (entries 23 and 24).

On the basis of kinetic studies half-sandwich imido compounds of the type (RHN)CpTi=NR have been proposed as the active species for the hydroamination of alkynes in the presence of titanium complexes containing η^5 ligands.[31] Under the catalysis, two major dangers threaten the active species: the reversible formation of tris(amide) derivatives, $CpTi(NHR)_3$, and the irreversible condensation of the catalysts into the dimers $(RHN)CpTi(\mu\text{-}NR)_2TiCp(NHR)$, which are catalytically inactive.

The higher efficiency of **4** with regard to **19** appears to be related to the fact that the pendant ether substituent of the cyclopentadienyl ligand of **4** exercises two protective effects on the active species. It can prevent the formation of both the tris(amide) and dimer compounds as a result of the reversible coordination of the oxygen atom to the metal center and/or as a consequence of its demand of space.

Concluding Remarks

This study has revealed that the pendant ether substituent of the (2-methoxyethyl)cyclopentadienyl ligand (Cp^O) has a strong influence on the stoichiometric and catalytic properties of its derivatives and that its behavior in half-sandwich titanium(IV) chemistry is determined by the coligands of the particular compound.

Complex Cp^OTiCl_3 reacts with 1.0, 2.0, and 3.0 equiv of MeMgCl to afford the mono-, di-, and trimethyl derivatives $Cp^OTiMeCl_2$, Cp^OTiMe_2Cl, and Cp^OTiMe_3, respectively. In the solid state, the pendant ether group of these compounds is bonded to the titanium atom, disposed transoid to a methyl ligand. In solution the ether dissociates, and an equilibrium between six- and seven-coordinate compounds is reached. The molar fraction of the dissociated ether species increases as the steric hindrance around the metal center grows. In agreement with this, the reactions of Cp^OTiCl_3 with 3.0 equiv of $PhCH_2MgCl$, PhMgCl, and (*p*-tolyl)MgBr lead to Cp^OTiR_3 (R = CH_2Ph, Ph, *p*-tolyl), with a free ether substituent in the solid state and in solution. The X-ray structure of Cp^OTiPh_3 shows clear evidence for a β-hydrogen agostic interaction between the metal center and one of the phenyl groups.

The pendant ether group is also free in the $Cp^OTiX_{3-n}(OAr)_n$ (X = Cl, CH_3; n = 1−3) aryloxide and unprecedented $Cp^OTiMe_n(OCPh_2C{\equiv}CH)_{3-n}$ (n = 1, 2) propargyloxide complexes. The X-ray structure of $Cp^OTi(O\text{-}2,6\text{-}{}^tBu_2\text{-}4\text{-}MeC_6H_2)Cl_2$ suggests a significant multiple-bond character for the Ti−O bond, in agreement with the π-donor power of the oxygen atom of the aryloxide and propargyloxide ligands.

The ether substituent of the cyclopentadienyl ligand influences the catalytic properties of Cp^OTiMe_3, which is more efficient than the related compound $CpTiMe_3$ containing an unsubstituted cyclopentadienyl ligand for the regioselective anti-Markovnikov hydroamination of phenylacetylene and internal alkynes with cyclohexylamine and 2,6-dimethylaniline.

In conclusion, we have reported the preparation and characterization of alkyl, aryl, aryloxide, and propargyloxide titanium complexes containing the (2-methoxyethyl)cyclopentadienyl ligand and analyzed the behavior of the pendant ether group of the new complexes in the solid state and in solution. In addition, we have shown that the introduction of an ether substituent in the cyclopentadienyl ligand increases the efficiency of the titanium cyclopentadienyl catalysts for the hydroamination of alkynes, in particular for those reactions involving the sterically less demanding substrates.

Experimental Section

General Methods and Instrumentation. All reactions were carried out under argon with rigorous exclusion of air using Schlenk-line or drybox techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The starting materials Cp^OTiCl_3 (**1**)[15c] and $CpTiMe_3$ (**19**)[32] were prepared by the published methods. Diphenylacetylene was dissolved in CH_2Cl_2, dried with Na_2SO_4, and recovered by evaporation of the solvent. Phenylacetylene and 1-phenylpropyne were distilled, and amines were distilled from CaH_2 and stored in the drybox. All other reagents were purchased from commercial sources and were used without further purification. The course of the catalytic reactions was followed using a Hewlett-Packard 5890 series gas chromatograph with a flame ionization detector, using a 100% cross-linked methylsilicone gum column (30 m × 0.25 mm, with 0.25 μm film thickness) and *n*-octane as the internal standard. The oven conditions used are as follows: 35 °C (hold 6 min) to 280 °C at 25 °C/min (hold 5 min). The reaction products were identified by GC-MS and by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. GC-MS experiments were run on an Agilent 5973 mass selective detector interfaced to an Agilent 6890 series gas chromatograph system. Samples were injected into a 30 m × 250 μm HP-5MS 5% phenylmethylsiloxane column with a film thickness of 0.25 μm (Agilent). The GC oven temperature was programmed as follows: 35 °C for 6 min to 280 °C at 25 °C/min for 5 min. The carrier gas was helium at a flow rate of 1 mL/min. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian UNITY 300, a Varian Gemini 2000, a Bruker AXR 300, or a Bruker Avance 400 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks). Coupling constants, *J*, are given in hertz. C and H analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer.

Preparation of $Cp^OTiMeCl_2$ (2). To an orange suspension of **1** (500 mg, 1.80 mmol) in 20 mL of diethyl ether at −40 °C was added dropwise 1.0 equiv of MeMgCl (0.60 mL, 1.80 mmol, 3 M in tetrahydrofuran). After addition, the mixture was warmed slowly to room temperature and stirred for 4 h. The volatiles were removed under reduced pressure, and the residue was extracted with pentane (3 × 50 mL). The resultant brown solution was concentrated to ca. 3 mL, and a brown solid appeared, which was separated by decantation, washed with 2 × 3 mL of pentane, and dried in vacuo. Yield: 180 mg (40%). Anal. Calcd for $C_9H_{14}Cl_2OTi$: C, 42.04; H, 5.50. Found: C, 42.39; H, 5.51. ^1H NMR (300 MHz, C_7D_8, 333 K): δ 6.09, 6.02 (both m, each 2H, C_5H_4), 3.11 (t, ^3J = 6.0, 2H, CH_2O), 3.08 (s, 3H, OMe), 2.38 (t, ^3J = 6.0, 2H, $C_5H_4CH_2$), 1.75 (s, 3H, TiMe). ^1H NMR (300 MHz, C_7D_8, 203 K): δ 6.15, 5.75 (both m, each 2H, C_5H_4), 3.26 (br s, 3H, OMe), 2.48 (m, 2H, CH_2O), 1.94 (br s, 3H, TiMe), 1.35 (m, 2H, $C_5H_4CH_2$). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_7D_8, 293 K, plus APT and HETCOR): δ 136.1

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(C_{ipso} C_5H_4), 119.6, 118.9 (C_5H_4), 79.5 (TiMe), 72.5 (CH_2O), 58.7 (OMe), 30.3 ($C_5H_4CH_2$). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_7D_8, 213 K, plus APT): δ 136.4 (C_{ipso} C_5H_4), 120.2, 118.5 (C_5H_4), 80.9 (TiMe), 75.2 (CH_2O), 59.9 (OMe), 27.0 ($C_5H_4CH_2$).

Preparation of Cp^OTiMe_2Cl (3). The same procedure described for **2** was followed, except that **1** (500 mg, 1.80 mmol) and 2.0 equiv of MeMgCl (1.20 mL, 3.60 mmol, 3 M in tetrahydrofuran) were used. The product was obtained as a red solid. Yield: 215 mg (50%). Anal. Calcd for $C_{10}H_{17}ClOTi$: C, 50.75; H, 7.25. Found: C, 51.05; H, 7.41. ^1H NMR (300 MHz, C_7D_8, 333 K): δ 5.97, 5.91 (both m, each 2H, C_5H_4), 3.19 (m, 2H, CH_2O), 3.09 (s, 3H, OMe), 2.36 (m, 2H, $C_5H_4CH_2$), 1.30 (s, 6H, $TiMe_2$). ^1H NMR (300 MHz, C_7D_8, 193 K): δ 6.07, 5.67 (both m, each 2H, C_5H_4), 3.20 (br s, 3H, OMe), 2.34 (m, 2H, CH_2O), 1.44 (m, 2H, $C_5H_4CH_2$), 1.29 (br s, 6H, $TiMe_2$). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_7D_8, 293 K, plus APT and HETCOR): δ 132.3 (C_{ipso} C_5H_4), 116.3, 115.2 (C_5H_4), 73.3 (CH_2O), 68.9 ($TiMe_2$), 58.6 (OMe), 30.0 ($C_5H_4CH_2$). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_7D_8, 213 K, plus APT): δ 133.3 (C_{ipso} C_5H_4), 117.4, 114.2 (C_5H_4), 76.8 (CH_2O), 68.5 ($TiMe_2$), 60.4 (OMe), 27.4 ($C_5H_4CH_2$).

Preparation of Cp^OTiMe_3 (4). The same procedure described for **2** was followed, except that **1** (493 mg, 1.77 mmol) and 3.0 equiv of MeMgCl (1.78 mL, 5.33 mmol, 3 M in tetrahydrofuran) were used. The product was obtained as an orange oil. Yield: 343 mg (89%). Anal. Calcd for $C_{11}H_{20}OTi$: C, 61.06; H, 9.37. Found: C, 61.10; H, 9.34. ^1H NMR (300 MHz, C_7D_8, 363 K): δ 5.91 (s, 4H, C_5H_4), 3.35 (t, ^3J = 6.0, 2H, CH_2O), 3.12 (s, 3H, OMe), 2.49 (t, ^3J = 6.0, 2H, $C_5H_4CH_2$), 1.14 (s, 9H, $TiMe_3$). ^1H NMR (300 MHz, C_7D_8, 183 K): δ 6.05, 5.59 (both m, each 2H, C_5H_4), 2.98 (br s, 3H, OMe), 2.49 (m, 2H, CH_2O), 1.71 (m, 2H, $C_5H_4CH_2$), 1.15 (br s, 9H, $TiMe_3$). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_7D_8, 293 K, plus APT and HETCOR): δ 129.5 (C_{ipso} C_5H_4), 113.5, 112.7 (C_5H_4), 73.2 (CH_2O), 62.0 ($TiMe_3$), 58.3 (OMe), 30.9 ($C_5H_4CH_2$). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_7D_8, 183 K, plus APT): δ 130.2 (C_{ipso} C_5H_4), 114.3, 111.8 (C_5H_4), 75.0 (CH_2O), 60.9 ($TiMe_3$), 59.0 (OMe), 29.5 ($C_5H_4CH_2$).

Preparation of $Cp^OTi(CH_2Ph)_3$ (5). The same procedure described for **2** was followed, except that **1** (419 mg, 1.51 mmol) and 3.0 equiv of $PhCH_2MgCl$ (2.26 mL, 4.53 mmol, 2 M in tetrahydrofuran) were used. The product was obtained as a red oil. Yield: 536 mg (80%). Anal. Calcd for $C_{29}H_{32}OTi$: C, 78.36; H, 7.27. Found: C, 78.22; H, 7.42. ^1H NMR (300 MHz, C_7D_8, 293 K): δ 7.15−6.77 (m, 15H, Ph), 5.66, 5.49 (both m, each 2H, C_5H_4), 3.12 (t, ^3J = 6.0, 2H, CH_2O), 3.01 (s, 3H, OMe), 2.96 (s, 6H, CH_2-Ph), 2.14 (t, ^3J = 6.0, 2H, $C_5H_4CH_2$). ^1H NMR (300 MHz, C_7D_8, 193 K): δ 7.22−6.76 (m, 15H, Ph), 5.57, 5.27 (both m, each 2H, C_5H_4), 3.09 (br s, 5H, CH_2O, OMe), 2.92 (br s, 6H, CH_2Ph), 1.82 (m, 2H, $C_5H_4CH_2$). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_7D_8, 293 K, plus APT): δ 148.6 (C_{ipso} Ph), 133.1 (C_{ipso} C_5H_4), 128.8, 126.7, 122.9 (Ph), 118.0, 116.6 (C_5H_4), 92.2 (CH_2Ph), 72.8 (CH_2O), 58.2 (OMe), 30.4 ($C_5H_4CH_2$). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_7D_8, 233 K, plus APT): δ 148.2 (C_{ipso} Ph), 133.4 (C_{ipso} C_5H_4), 128.8, 126.5, 122.9 (Ph), 118.1, 116.6 (C_5H_4), 91.9 (CH_2Ph), 72.7 (CH_2O), 58.2 (OMe), 30.2 ($C_5H_4CH_2$).

Preparation of Cp^OTiPh_3 (6). An orange suspension of **1** (315 mg, 1.13 mmol) in 18 mL of diethyl ether was treated with 3.0 equiv of PhMgCl (1.70 mL, 3.41 mmol, 2 M in tetrahydrofuran) added dropwise at −50 °C. After addition, the mixture was stirred for 4 h at −30 °C. The volatiles were removed under reduced pressure, and the residue was extracted with pentane (4 × 40 mL). The resultant yellow solution was concentrated to ca. 3 mL and kept at −78 °C for 15 h. After that, a greenish yellow solid appeared, which was separated by decantation and dried in vacuo. Yield: 182 mg (40%). Anal. Calcd for $C_{26}H_{26}OTi$: C, 77.60; H, 6.52. Found: C, 77.33; H, 6.55. ^1H NMR (300 MHz, CD_2Cl_2, 183 K): δ 7.61−7.14 (m, 15H, Ph), 6.76, 6.58 (both m, each 2H, C_5H_4), 3.39 (t, ^3J = 6.0, 2H, CH_2O), 3.21 (s, 3H, OMe), 2.32 (t, ^3J = 6.0, 2H, $C_5H_4CH_2$). ^{13}C NMR (75.42 MHz, CD_2Cl_2, 183 K): δ 198.3 (t, $^2J_{CH}$ = 6, C_{ipso} Ph), 132.2 (m, C_{ipso} C_5H_4), 132.1 (dt, $^1J_{CH}$ = 156, $^2J_{CH}$ = 6, *m*-Ph), 129.2 (dt, $^1J_{CH}$ = 156, $^2J_{CH}$ = 6, *p*-Ph), 126.1 (dd, $^1J_{CH}$ = 156, $^2J_{CH}$ = 6, *o*-Ph), 117.9, 115.6 (both m, C_5H_4), 72.5 (t, $^1J_{CH}$ = 142, CH_2O), 58.2 (q, $^1J_{CH}$ = 142, OMe), 30.7 (t, $^1J_{CH}$ = 142, $C_5H_4CH_2$).

Preparation of $Cp^OTi(p\text{-tolyl})_3$ (7). The same procedure described for **6** was followed, except that **1** (496 mg, 1.79 mmol) and 3.0 equiv of (*p*-tolyl)MgBr (5.40 mL, 5.37 mmol, 1 M in tetrahydrofuran) were used. The product was obtained as a green oil. Yield: 295 mg (37%). Anal. Calcd for $C_{29}H_{32}OTi$: C, 78.36; H, 7.27. Found: C, 78.84; H, 7.79. ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.55, 7.00 (both d, ^3J = 7.5, 6H, $CH_3C_6H_4$), 6.74, 6.59 (both m, each 2H, C_5H_4), 3.45 (t, ^3J = 6.0, 2H, CH_2O), 3.29 (s, 3H, OMe), 2.43 (t, ^3J = 6.0, 2H, $C_5H_4CH_2$), 2.31 (s, 9H, $CH_3C_6H_4$). $^{13}C\{^1H\}$ NMR (75.42 MHz, CD_2Cl_2, 223 K, plus APT): δ 197.8 (C_{ipso} C_6H_4), 139.1 (*p*-$CH_3C_6H_4$), 133.5 (*m*-$CH_3C_6H_4$), 135.0 (C_{ipso} C_5H_4), 127.5 (*o*-$CH_3C_6H_4$), 117.7, 116.9 (C_5H_4), 73.5 (CH_2O), 59.1 (OMe), 31.8 ($C_5H_4CH_2$), 22.1 (*p*-$CH_3C_6H_4$).

Preparation of $Cp^OTi(O\text{-}2,6\text{-}{}^tBu_2\text{-}4\text{-}MeC_6H_2)Cl_2$ (8). To an orange suspension of **1** (500 mg, 1.80 mmol) in 15 mL of diethyl ether at −30 °C was added a precooled (−30 °C) solution of Li(O-2,6-^{t}Bu$_2$-4-MeC_6H_2) (408 mg, 1.80 mmol) in 10 mL of diethyl ether. After addition, the mixture was warmed slowly to room temperature and stirred overnight. The mixture was filtered, and the resultant red solution was concentrated to ca. 3 mL and kept at −78 °C for 15 h. After that, a red solid appeared, which was separated by decantation and dried in vacuo. Yield: 635 mg (76%). Anal. Calcd for $C_{23}H_{34}Cl_2O_2Ti$: C, 59.88; H, 7.43. Found: C, 59.94; H, 7.25. ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.05 (s, 2H, C_6H_2), 6.32, 5.91 (both m, each 2H, C_5H_4), 3.27 (t, ^3J = 6.0, 2H, CH_2O), 2.98 (s, 3H, OMe), 2.96 (t, ^3J = 6.0, 2H, $C_5H_4CH_2$), 2.18 (s, 3H, $CH_3C_6H_2$), 1.47 (s, 18H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 169.3 (Ti−O−C), 139.7 (*o*-C_6H_2), 138.7 (*p*-C_6H_2), 131.8 (C_{ipso} C_5H_4), 126.3 (*m*-C_6H_2), 122.5, 120.6 (C_5H_4), 71.5 (CH_2O), 58.0 (OMe), 35.7 ($C(CH_3)_3$), 31.8 ($C(CH_3)_3$), 30.2 ($C_5H_4CH_2$), 21.0 ($CH_3C_6H_2$).

Preparation of $Cp^OTiMe(O\text{-}2,6\text{-}{}^tBu_2\text{-}4\text{-}MeC_6H_2)Cl$ (9). To a red solution of **8** (274 mg, 0.59 mmol) in 15 mL of diethyl ether at −40 °C was added dropwise 1.0 equiv of MeMgCl (0.20 mL, 0.59 mmol, 3 M in tetrahydrofuran). After addition, the mixture was warmed slowly to room temperature and stirred for 10 h. The volatiles were removed under reduced pressure, and the residue was extracted with pentane (2 × 25 mL). The resultant orange solution was removed under vacuum, affording an orange oil. Yield: 180 mg (69%). Anal. Calcd for $C_{24}H_{37}ClO_2Ti$: C, 65.36; H, 8.47. Found: C, 65.82; H, 9.08. ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.10 (s, 2H, C_6H_2), 6.39, 5.90, 5.86, 5.57 (all m, each 1H, C_5H_4), 3.31 (t, ^3J = 6.3, 2H, CH_2O), 3.04 (s, 3H, OMe), 2.85 (t, ^3J = 6.3, 2H, $C_5H_4CH_2$), 2.22 (s, 3H, $CH_3C_6H_2$), 1.64 (s, 3H, TiMe), 1.45 (s, 18H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 166.2 (Ti−O−C), 139.5 (*o*-C_6H_2), 130.3 (*p*-C_6H_2), 129.2 (C_{ipso} C_5H_4), 126.1 (*m*-C_6H_2), 119.2, 117.5, 115.7, (C_5H_4), 72.4 (CH_2O), 67.4 (TiMe), 58.2 (OMe), 35.6 ($C(CH_3)_3$), 31.9 ($C(CH_3)_3$), 31.4 ($C_5H_4CH_2$), 21.3 ($CH_3C_6H_2$).

Preparation of $Cp^OTiMe_2(O\text{-}2,6\text{-}{}^tBu_2\text{-}4\text{-}MeC_6H_2)$ (10). Method 1. The same procedure described for **9** was followed, except that **8** (267 mg, 0.58 mmol) and 2.0 equiv of MeMgCl (0.38 mL, 1.16 mmol, 3 M in tetrahydrofuran) were used. The product was obtained as a yellow oil. Yield: 146 mg (60%).

Method 2. The same procedure described for **9** was followed, except that **9** (70 mg, 0,16 mmol) and 1.0 equiv of MeMgCl (0.05 mL, 0.16 mmol, 3 M in tetrahydrofuran) were used. Yield: 50 mg (75%). Anal. Calcd for $C_{25}H_{40}O_2Ti$: C, 71.40; H, 9.61. Found: C, 71.33; H, 9.82. ^1H NMR (300 MHz, C_7D_8, 293 K): δ 7.08 (s, 2H, C_6H_2), 5.99, 5.59 (both m, each 2H, C_5H_4), 3.36 (t, ^3J = 6.0, 2H, CH_2O), 3.01 (s, 3H, OMe), 2.70 (t, ^3J = 6.0, 2H, $C_5H_4CH_2$), 2.24

(s, 3H, CH_3C$_6$H$_2$), 1.40 (s, 18H, C(CH$_3$)$_3$), 0.95 (s, 6H, TiMe$_2$). ^{13}C{^{1}H} NMR (75.42 MHz, C_7D_8, 293 K, plus APT): δ 164.7 (Ti−O−C), 139.5 (*o*-C$_6$H$_2$), 129.2 (*p*-C$_6$H$_2$), 129.1 (C$_{ipso}$ C$_5$H$_4$), 126.1 (*m*-C$_6$H$_2$), 116.1, 113.8 (C$_5$H$_4$), 73.5 (CH$_2$O), 60.8 (TiMe$_2$), 58.4 (OMe), 35.6 (*C*(CH$_3$)$_3$), 31.8 (C(*C*H$_3$)$_3$), 31.2 (C$_5$H$_4$*C*H$_2$), 21.5 (*C*H$_3$C$_6$H$_2$).

Preparation of Cp^{O}Ti(O-2,6-^{i}Pr$_2$C$_6$H$_3$)Cl$_2$ (11). The same procedure described for **8** was followed, except that **1** (1090 mg, 3.93 mmol) and a solution of Li(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (720 mg, 3.93 mmol) were used. The product was obtained as a reddish orange solid. Yield: 1.54 g (93%). Anal. Calcd for $C_{20}H_{28}Cl_2O_2Ti$: C, 57.30; H, 6.75. Found: C, 56.95; H, 6.73. ^{1}H NMR (300 MHz, C_7D_8, 293 K): δ 7.00−6.93 (m, 3H, C$_6$H$_3$), 6.23, 5.97 (both m, each 2H, C$_5$H$_4$), 3.39 (sept, ^3J = 6.9, 2H, C*H*(CH$_3$)$_2$), 3.22 (t, ^3J = 6.0, 2H, CH$_2$O), 2.97 (s, 3H, OMe), 2.84 (t, ^3J = 6.0, 2H, C$_5$H$_4$C*H*$_2$), 1.22 (d, ^3J = 6.9, 12H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (75.42 MHz, C_7D_8, 293 K, plus APT): δ 164.5 (Ti−O−C), 138.6 (*o*-C$_6$H$_3$), 138.4 (C$_{ipso}$ C$_5$H$_4$), 124.8 (*p*-C$_6$H$_2$), 123.7 (*m*-C$_6$H$_2$), 121.2, 119.9 (C$_5$H$_4$), 71.6 (CH$_2$O), 58.2 (OMe), 31.5 (C$_5$H$_4$*C*H$_2$), 27.2 (*C*H(CH$_3$)$_2$), 23.7 (CH(*C*H$_3$)$_2$).

Preparation of Cp^{O}Ti(O-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$Cl (12). The same procedure described for **8** was followed, except that **1** (524 mg, 1.90 mmol) and a solution of Li(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (700 mg, 3.80 mmol) were used. The product was obtained as a yellow oil. Yield: 202 mg (45%). Anal. Calcd for $C_{32}H_{45}ClO_3Ti$: C, 68.48; H, 8.10. Found: C, 68.72; H, 8.35. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 7.11−6.94 (m, 6H, C$_6$H$_3$), 6.23, 6.10 (both m, each 2H, C$_5$H$_4$), 3.72 (sept, ^3J = 6.9, 4H, C*H*(CH$_3$)$_2$), 3.21 (t, ^3J = 6.0, 2H, CH$_2$O), 2.97 (t, ^3J = 6.0, 2H, C$_5$H$_4$C*H*$_2$), 2.93 (s, 3H, OMe), 1.28, 1.24 (both d, ^3J = 6.9, each 12H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 163.7 (Ti−O−C), 138.0 (*o*-C$_6$H$_3$), 136.6 (C$_{ipso}$ C$_5$H$_4$), 123.7 (*m*-C$_6$H$_3$), 123.5 (*p*-C$_6$H$_3$), 119.4, 117.7 (C$_5$H$_4$), 71.9 (CH$_2$O), 58.0 (OMe), 31.1 (C$_5$H$_4$*C*H$_2$), 26.7 (*C*H(CH$_3$)$_2$), 24.2, 23.6 (CH(*C*H$_3$)$_2$).

Preparation of Cp^{O}Ti(O-2,6-^{i}Pr$_2$C$_6$H$_3$)$_3$ (13). The same procedure described for **8** was followed, except that **1** (450 mg, 1.62 mmol) and a solution of Li(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (896 mg, 4.87 mmol) were used. The product was obtained as an orange oil. Yield: 395 mg (35%). Anal. Calcd for $C_{44}H_{62}O_4Ti$: C, 75.17; H, 8.91. Found: C, 75.22; H, 9.06. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 7.13−6.82 (m, 9H, C$_6$H$_3$), 6.07, 6.01 (both m, each 2H, C$_5$H$_4$), 3.67 (sept, ^3J = 6.9, 6H, C*H*(CH$_3$)$_2$), 3.11 (t, ^3J = 6.0, 2H, CH$_2$O), 2.79 (t, ^3J = 6.0, 2H, C$_5$H$_4$C*H*$_2$), 2.72 (s, 3H, OMe), 1.27 (d, ^3J = 6.9, 36H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 163.7 (Ti−O−C), 138.0 (*o*-C$_6$H$_3$), 134.7 (C$_{ipso}$ C$_5$H$_4$), 123.7 (*m*-C$_6$H$_3$), 123.4 (*p*-C$_6$H$_3$), 119.0, 117.7 (C$_5$H$_4$), 72.0 (CH$_2$O), 57.7 (OMe), 29.8 (C$_5$H$_4$*C*H$_2$), 26.7 (*C*H(CH$_3$)$_2$), 24.2 (CH(*C*H$_3$)$_2$).

Preparation of Cp^{O}TiMe(O-2,6-^{i}Pr$_2$C$_6$H$_3$)Cl (14). The same procedure described for **9** was followed, except that **11** (337 mg, 0.80 mmol) and 1.0 equiv of MeMgCl (0.27 mL, 0.80 mmol, 3 M in tetrahydrofuran) were used. The product was obtained as an orange oil. Yield: 221 mg (84%). Anal. Calcd for $C_{21}H_{31}ClO_2Ti$: C, 63.22; H, 7.85. Found: C, 63.68; H, 8.26. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 7.12−6.94 (m, 3H, C$_6$H$_3$), 6.24, 5.93, 5.91, 5.68 (both m, each 1H, C$_5$H$_4$), 3.33 (sept, ^3J = 6.9, 2H, C*H*(CH$_3$)$_2$), 3.22 (t, ^3J = 6.3, 2H, CH$_2$O), 2.99 (s, 3H, OMe), 2.70 (t, ^3J = 6.3, 2H, C$_5$H$_4$C*H*$_2$), 1.52 (s, 3H, TiMe), 1.26, 1.20 (both d, ^3J = 6.9, each 6H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 162.1 (Ti−O−C), 138.1 (*o*-C$_6$H$_3$), 132.9 (C$_{ipso}$ C$_5$H$_4$), 123.6 (*m*-C$_6$H$_3$), 123.4 (*p*-C$_6$H$_3$), 117.8, 116.7, 116.1, 115.5 (C$_5$H$_4$), 72.3 (CH$_2$O), 61.3 (TiMe), 58.3 (OMe), 31.0 (C$_5$H$_4$*C*H$_2$), 27.2 (*C*H(CH$_3$)$_2$), 23.8, 23.7 (CH(*C*H$_3$)$_2$).

Preparation of Cp^{O}TiMe$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (15). Method 1. The same procedure described for **9** was followed, except that **11** (528 mg, 1.26 mmol) and 2.0 equiv of MeMgCl (0.84 mL, 2.52 mmol, 3 M in tetrahydrofuran) were used. The product was obtained as a yellow oil. Yield: 468 mg (98%).

Method 2. An orange solution of **4** (250 mg, 1.16 mmol) in 10 mL of diethyl ether was treated with 1.0 equiv of HO(2,6-^{i}Pr$_2$C$_6$H$_3$) (206 mg, 1.16 mmol) at −15 °C. Immediately methane evolution was observed. The mixture was warmed to room temperature and stirred for 2 h. Then, the solvent was removed under vacuum. Yield: 345 mg (79%). Anal. Calcd for $C_{22}H_{34}O_2Ti$: C, 69.82; H, 9.07. Found: C, 69.65; H, 9.13. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 7.12−6.96 (m, 3H, C$_6$H$_3$), 5.96, 5.77 (both m, each 2H, C$_5$H$_4$), 3.36 (sept, ^3J = 6.9, 2H, C*H*(CH$_3$)$_2$), 3.27 (t, ^3J = 6.6, 2H, CH$_2$O), 3.02 (s, 3H, OMe), 2.58 (t, ^3J = 6.6, 2H, C$_5$H$_4$C*H*$_2$), 1.24 (d, ^3J = 6.9, 12H, CH(C*H*$_3$)$_2$), 0.94 (s, 6H, TiMe$_2$). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 160.9 (Ti−O−C), 138.1 (*o*-C$_6$H$_3$), 129.2 (C$_{ipso}$ C$_5$H$_4$), 123.4 (*m*-C$_6$H$_3$), 122.3 (*p*-C$_6$H$_3$), 113.4, 112.9 (C$_5$H$_4$), 72.9 (CH$_2$O), 58.3 (OMe), 54.1 (TiMe$_2$), 30.7 (C$_5$H$_4$*C*H$_2$), 26.8 (*C*H(CH$_3$)$_2$), 23.7 (CH(*C*H$_3$)$_2$).

Preparation of Cp^{O}TiMe(O-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$ (16). Method 1. The same procedure described for **9** was followed, except that **12** (202 mg, 0.36 mmol) and 1.0 equiv of MeMgCl (0.12 mL, 0.36 mmol, 3 M in tetrahydrofuran) were used. The product was obtained as an orange oil. Yield: 134 mg (69%).

Method 2. The same procedure described for **15** was followed, except that **4** (104 mg, 0.48 mmol) and 2.0 equiv of HO(2,6-^{i}Pr$_2$C$_6$H$_3$) (171 mg, 0.96 mmol) were used. Yield: 142 mg (55%). Anal. Calcd for $C_{33}H_{48}O_3Ti$: C, 73.30; H, 8.97. Found: C, 73.18; H, 9.04. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 7.12−6.93 (m, 6H, C$_6$H$_3$), 6.08, 5.96 (both m, each 2H, C$_5$H$_4$), 3.54 (sept, ^3J = 6.9, 4H, C*H*(CH$_3$)$_2$), 3.17 (t, ^3J = 6.0, 2H, CH$_2$O), 2.97 (s, 3H, OMe), 2.65 (t, ^3J = 6.0, 2H, C$_5$H$_4$C*H*$_2$), 1.40 (s, 3H, TiMe), 1.23, 1.21 (both d, ^3J = 6.9, each 12H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 161.4 (Ti−O−C), 137.7 (*o*-C$_6$H$_3$), 130.2 (C$_{ipso}$ C$_5$H$_4$), 123.5 (*m*-C$_6$H$_3$), 122.2 (*p*-C$_6$H$_3$), 115.4, 113.6 (C$_5$H$_4$), 72.6 (CH$_2$O), 58.1 (OMe), 48.5 (TiMe), 30.2 (C$_5$H$_4$*C*H$_2$), 26.6 (*C*H(CH$_3$)$_2$), 23.9, 23.6 (CH(*C*H$_3$)$_2$).

Preparation of Cp^{O}TiMe$_2$(OCPh$_2$C≡CH) (17). An orange solution of **4** (366 mg, 1.70 mmol) in 15 mL of tetrahydrofuran was treated with 1.0 equiv of HOCPh$_2$C≡CH (353 mg, 1.70 mmol) at −15 °C. Immediately methane evolution was observed. The mixture was warmed slowly to room temperature and stirred for 2 h. Then, the solvent was removed under vacuum and a green oil was obtained. The product was washed with pentane (3 × 3 mL), which was isolated as a green oil. Yield: 650 mg (94%). Anal. Calcd for $C_{25}H_{28}O_2Ti$: C, 73.51; H, 6.92. Found: C, 73.32; H, 7.01. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 7.92−6.99 (m, 10H, Ph), 5.99, 5.73 (both m, each 2H, C$_5$H$_4$), 3.28 (t, ^3J = 6.0, 2H, CH$_2$O), 3.04 (s, 3H, OMe), 2.58 (t, ^3J = 6.0, 2H, C$_5$H$_4$C*H*$_2$), 2.31 (s, 1H, ≡CH), 0.84 (s, 6H, TiMe$_2$). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 146.8 (C$_{ipso}$ Ph), 129.4 (C$_{ipso}$ C$_5$H$_4$), 128.5 (*m*-Ph), 127.8 (*p*-Ph), 126.5 (*o*-Ph), 113.9, 112.9 (C$_5$H$_4$), 87.4 (*C*Ph$_2$), 85.7 (*C*≡CH), 75.2 (C≡*C*H), 73.0 (CH$_2$O), 58.2 (OMe), 52.5 (TiMe$_2$), 30.7 (C$_5$H$_4$*C*H$_2$).

Preparation of Cp^{O}TiMe(OCPh$_2$C≡CH)$_2$ (18). The same procedure described for **17** was followed, except that **4** (465 mg, 2.15 mmol) and 2.0 equiv of HOCPh$_2$C≡CH (897 mg, 4.31 mmol) were used. The product was obtained as a light yellow solid. Yield: 547 mg (42%). Anal. Calcd for $C_{39}H_{36}O_3Ti$: C, 77.98; H, 6.05. Found: C, 77.68; H, 5.93. ^{1}H NMR (300 MHz, C_7D_8, 293 K): δ 7.78−7.00 (m, 20H, Ph), 6.05, 5.89 (both m, each 2H, C$_5$H$_4$), 3.21 (t, ^3J = 6.0, 2H, CH$_2$O), 3.02 (s, 3H, OMe), 2.58 (t, ^3J = 6.0, 2H, C$_5$H$_4$C*H*$_2$), 2.36 (s, 2H, ≡CH), 1.13 (s, 3H, TiMe). ^{13}C{^{1}H} NMR (75.42 MHz, C_7D_8, 293 K, plus APT and HETCOR): δ 147.2, 147.1 (C$_{ipso}$ Ph), 129.2 (C$_{ipso}$ C$_5$H$_4$), 128.3, 127.6, 126.7, 126.6 (Ph), 114.3, 112.8 (C$_5$H$_4$), 87.5 (*C*Ph$_2$), 85.3 (*C*≡CH), 75.2 (C≡*C*H), 73.0 (CH$_2$O), 58.2 (OMe), 45.9 (TiMe), 30.4 (C$_5$H$_4$*C*H$_2$).

Determination of Constants and Thermodynamic Parameters for the Equilibriums Shown in Eq 1. Variable-temperature ^{1}H NMR spectra of **2** (203−333 K), **3** (193−333 K), and **4** (183−363 K) were recorded in toluene-d_8. Equilibrium constants, *K*, were der-

Table 6. Crystal Data and Data Collection and Refinement Details for 2, 3, 6, and 8

	2	3	6	8
		Crystal Data		
formula	$C_9H_{14}Cl_2OTi$	$C_{10}H_{17}ClOTi$	$C_{26}H_{26}OTi$	$C_{23}H_{34}Cl_2O_2Ti$
mol wt	257.00	236.59	402.37	461.30
color, habit	orange, irregular block	red, irregular block	yellow, plate	orange, irregular block
size, mm	0.20 × 0.12 × 0.10	0.40 × 0.38 × 0.30	0.14 × 0.10 × 0.04	0.24 × 0.22 × 0.12
symmetry, space group	monoclinic, $P2_1$	monoclinic, $P2_1/c$	monoclinic, $P2_1/n$	monoclinic, $P2_1/c$
a, Å	6.8794(6)	7.4633(6)	13.071(2)	20.191(4)
b, Å	9.2704(8)	11.2428(9)	9.8025(15)	10.3853(17)
c, Å	9.0919(8)	13.7705(11)	15.986(2)	11.541(2)
β, deg	109.0610(10)	103.666(2)	93.739(3)	100.225(3)
V, Å^3	548.04(8)	1122.75(16)	2044.0(5)	2381.6(8)
Z	2	4	4	4
D_{calcd}, g cm^{-3}	1.557	1.400	1.308	1.287
		Data Collection and Refinement		
diffractometer		Bruker Smart APEX		
λ(Mo Kα), Å		0.71073		
monochromator		graphite oriented		
scan type		ω scans		
μ, mm^{-1}	1.226	0.961	0.432	0.599
2θ range, deg		3−57		
temp, K		100.0(2)		
no. of data collect	6739	13 462	13 176	20 777
no. of unique data	2597 (R_{int} = 0.0232)	2743 (R_{int} = 0.0326)	4865 (R_{int} = 0.1012)	5770 (R_{int} = 0.0640)
no. of params/restraints	121/31	186/0	254/0	261/0
R1[a] ($F^2 > 2\sigma(F^2)$)	0.0361	0.0266	0.0544	0.0451
wR2[b] (all data)	0.0856	0.0558	0.0973	0.0892
S[c] (all data)	1.013	0.984	0.762	0.859

[a] $R1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] GOF $= S = \{\sum[(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

ived from the temperature-dependent $\delta(^1H)$ values of the methylene signals CpCH_2 and OCH_2 using eq 2. Thermodynamic parameters were calculated from the equilibrium constants according to eq 5.

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (5)$$

Reasonable values for δ_{min} and δ_{max} were obtained by computer-assisted iteration: δ_{min} and δ_{max} were optimized in such a way that plotting of ln K versus $1/T$ gives the straightest line possible.

General Procedure for Hydroamination. A Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar was charged with the alkyne (2.40 mmol), the amine (2.64 mmol), complex **4** or complex **19** (0.12 mmol, 5.0% mol), toluene (2 mL), and *n*-octane (2.40 mmol). The Schlenk was removed from the glovebox and heated at 100 °C. The reaction was monitored by periodic GC analysis of samples removed with a syringe. Either on completion of the reaction or after 8 h, the volatiles were removed under reduced pressure and the residue was analyzed by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and by GC-MS. Imines and enamines were identified by comparison of their NMR spectra with their literature reported data.[19]

General Procedure for Hydrogenation. In a Fischer−Porter bottle, PtO_2 (15 mg, 0.07 mmol) was stirred in tetrahydrofuran (3.0 mL) at 25 °C under 1 atm of H_2 for 10 min. A solution of the crude hydroamination product in tetrahydrofuran (3.0 mL) was then added. The resulting mixture was stirred under 3 atm of H_2 at 25 °C for 48 h. Filtration, concentration, and purification by flash chromatography on silica gel afforded the amines, whose purity was checked by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and by GC-MS. Amines were identified by comparison of their NMR spectra with their literature reported data.[19]

Structural Analysis of Complexes 2, 3, 6, 8, and 18. A summary of crystal data and data collection and refinement details is reported in Table 6. X-ray data were collected for all complexes at low temperature on a Bruker Smart APEX CCD diffractometer at 100.0(2) K equipped with a normal-focus, 2.4 kW sealed-tube source (Mo radiation, λ = 0.710 73 Å) operating at 50 kV and 40 mA. Data were collected over the complete sphere by a combination of four sets. Each frame exposure time was 10 or 30 s covering 0.3° in ω. Data were corrected for absorption by using a multiscan method applied with the SADABS program.[33] The structures for all compounds were solved by the Patterson method. Refinements, by full-matrix least squares on F^2 with SHELXL97,[34] were similar for all complexes, including isotropic and subsequently anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms were observed or calculated and refined freely or refined using a restricted riding model, respectively.

For **2**, the systematic absences were consistent with space groups $P2_1$ and $P2_1/m$, but in the latter group the mirror plane would imply a nonobserved disorder in the Cp ligand. In the last cycles of refinement a "rigid bond" [SHELXL-DELU] restraint was used to the five carbon atoms of the Cp group.

We have tried unsuccessfully to obtain good-quality data for complex **18**. Unfortunately, the instability of the crystals only allows us to show the stereochemistry of the complex but not to discuss the structural parameters. Crystal data for **18**: $C_{39}H_{36}O_3Ti$; mol wt 600.58; monoclinic, $P2_1/c$; a = 30.862(5) Å, b = 11.989(5) Å, c = 16.960(5) Å, β = 95.438(5)°; V = 6247(3) Å^3; Z = 8; D_{calcd} = 1.277 g cm^{-3}; μ = 0.3 mm^{-1}; 2θ range 3−57°; temperature 100 K; 25 416 data collected; 8152 unique data (R_{int} = 0.14); R1($F^2 > 2\sigma(F^2)$) = 0.23 (isotropic model).

Acknowledgment. Financial support from the MCYT of Spain (Project CTQ2005-00656 and PPQ2000-0488-P4-02) is acknowledged. A.C.M. thanks Repsol-YPF for a grant.

Supporting Information Available: CIF files giving crystal data for compounds **2**, **3**, **6,** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM051031B

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