# Synthesis and Reactivity of a Titanocene–Benzyne Complex

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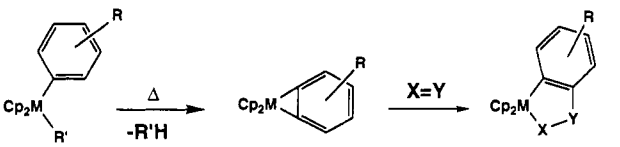
The thermolysis of (2-methoxyphenyl)methyltitanocene (**2**) in the presence of various unsaturated substrates regioselectively to yield metallacycles, presumably *via* the intermediacy of the titanocene–benzyne complex **3**, is described. If the thermolysis is effected in the presence of trimethylphosphine, the titanocene–benzyne complex $Cp_2Ti(\eta^2\text{-}C_6H_4\text{-}2\text{-}OMe)(PMe_3)$ (**1a**) can be isolated. The reactions of **1a** and **3** are compared to those of the analogous zirconium complexes.

## Introduction

For several years, our group has been interested in the development of new strategies for the utilization of organozirconium complexes as reagents in organic synthesis. The use of aryne complexes of zirconocene has proved to be very versatile, allowing for the synthesis of a wide range of organic compounds.[1] Zirconocene complexes of arynes were originally generated by thermal decomposition of diarylzirconocene derivatives[2] and trapped by reaction with unsaturated substrates to afford the corresponding metallacycles (Scheme I). Subsequently, we developed a strategy which involved the use of methyl(aryl)- rather than bis(aryl)zirconocene complexes as precursors.[3] This allowed the use of *ortho*-substituted aryl groups as an improved means for the generation of 3-substituted aryne complexes.[2c] In addition, we showed that the aryne complexes could be isolated as their trimethylphosphine adducts and that these stabilized complexes also reacted with unsaturated reagents, usually at room temperature. The reaction of *ortho*-substituted aryne ligands with unsaturated substrates was quite selective, usually leading to only one of the possible isomeric metallacyclic products in high yield.[9]

While there have been several studies, both mechanistic and synthetic, on analogous titanocene complexes,[4-8] we felt that a more detailed comparison of the chemistry of these titanium complexes and their zirconium analogs would be worthwhile. Herein we report some results of this study.

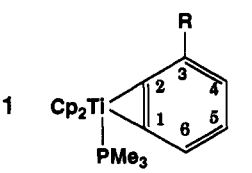
**Scheme I**




R' = $RC_4H_6$, $CH_3$
M = Zr, Ti

## Results and Discussion

In view of the zirconocene chemistry studied in these laboratories, we were interested in the synthesis of complexes of type 1, in order to compare their chemistry to that of their zirconium analogs. In agreement with




previous reports,[10] we were unable to isolate 2,2′-disubstituted diaryltitanocene derivatives, which would be precursors for complexes of type 1. As mentioned above, in the zirconium case, the problem was solved by using methyl(aryl)- rather than bis(aryl)metallocene precursors.[11] We therefore attempted to prepare the analogous titanium complexes. However, the isolation of such complexes proved to be troublesome, since the reaction of $Cp_2Ti(Me)Cl$ with aryllithium reagents usually led to mixtures of products.[12] Although in general the reaction of $Cp_2Ti(Me)Cl$ with an aryllithium species was not a suitable method for the preparation of methyl(aryl)-titanocene complexes, we found it useful in some specific

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(4) (a) Masai, H.; Sonogashira, K.; Haghiara, K. *Bull. Soc. Chem. Jpn.* **1968**, *41*, 750. (b) Dvorak, J.; O'Brien, R. I.; Santo, W. *J. Chem. Soc. D* **1970**, 411.

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(10) Summers, L.; Uloth, R. H.; Holmes, A. *J. Am. Chem. Soc.* **1955**, *77*, 3604.

(11) During the preparation of this paper, the analogous thermolysis of $Cp^*_2Ti(Ph)(Me)$ and subsequent trapping of the intermediate benzyne complex with $CO_2$ was reported: Teuben, J. H.; Luinstra, G. A. *Organometallics* **1992**, *11*, 1793.

(12) Puddephatt, R. J.; Stalteri, M. *Organometallics* **1983**, *2*, 1400.

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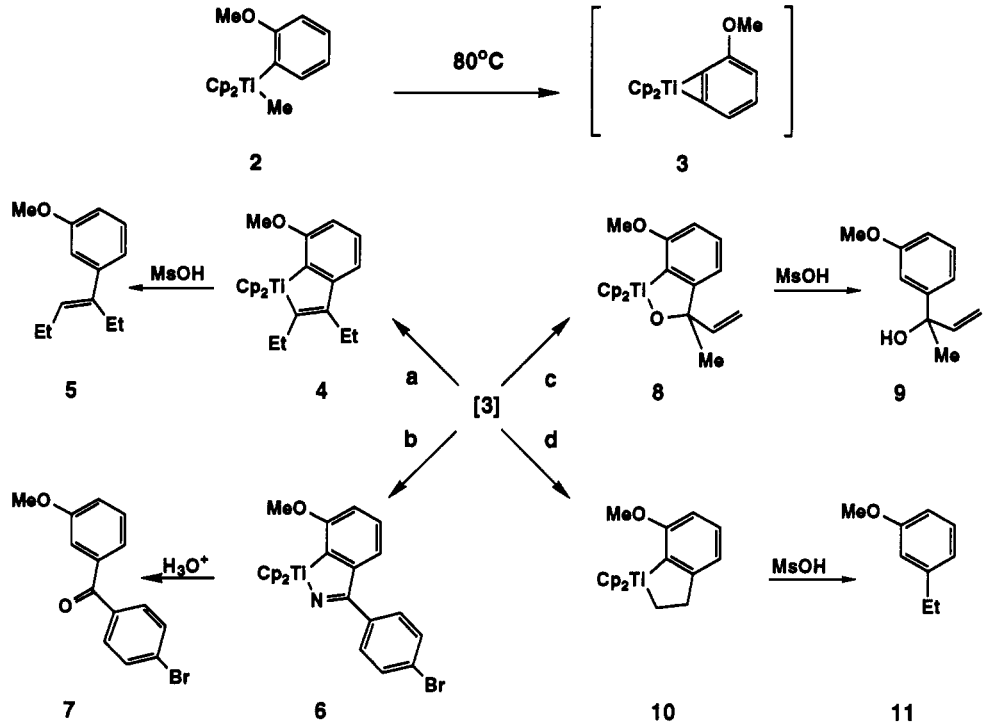
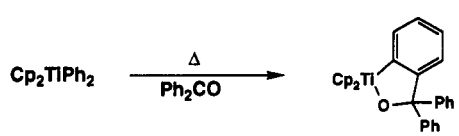
**Scheme II**[a]




[a] Legend: (a) EtC≡CEt; (b) *p*-$BrC_6H_4CN$; (c) $MeCOCH{=}CH_2$; (d) $C_2H_4$.

cases. Thus, reaction of (2-methoxyphenyl)lithium with $Cp_2Ti(Me)Cl$ afforded $Cp_2Ti(Me)(C_6H_4$-*o*-OMe) (**2**) in 65% isolated yield. That **2** could serve as a precursor to the 3-methoxybenzyne complex of titanocene **3** was evidenced by the fact that its thermolysis in the presence of various substrates provided the metallacyclic products expected from trapping of **3**. As shown in Scheme II, **3**, generated in an *in situ* manner, reacts regioselectively with a variety of unsaturated organic substrates. Consistent with what has been previously reported,[4a] heating **2** in the presence of 3-hexyne gives **4**, as a single regioisomer. Protonolysis of **4** with methanesulfonic acid leads to **5**, showing that the alkyne inserted selectively into the Ti–C(1) bond of **3**. This selectivity is identical with that seen by Rausch and Mintz[8a] and in the analogous zirconium case.[9a] It is probably due to the greater steric hindrance in the approach of the alkyne *syn* to the methoxy group and, as can be seen in Scheme II, is displayed with a range of different substrates. For example, reaction of *p*-bromobenzonitrile with **3** affords exclusively the metallacycle **6**, as confirmed by its hydrolysis to the *meta*-substituted anisole derivative **7**.

Thermolysis of $Cp_2TiPh_2$ in the presence of benzophenone has been reported to yield the corresponding titanacycle **12** (eq 1).[7] This is of interest, since the

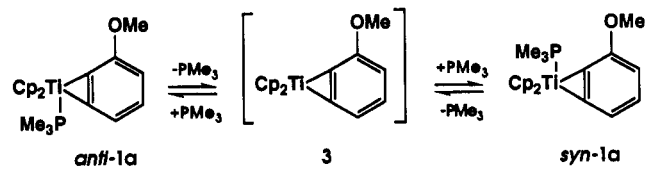



(1)

**12**

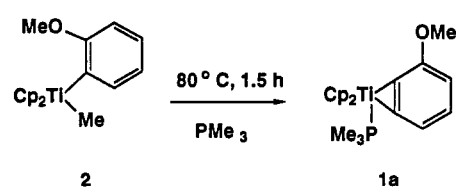
analogous zirconacycles were not formed when $Cp_2ZrPh_2$ and $Cp_2Zr(Me)Ar$ were heated in the presence of ketones.[1] These oxametallacycles could, however, be prepared from the $PMe_3$-stabilized aryne complexes.[1] As shown in Scheme II, the thermolysis of **2** in the presence of 1 equiv of methyl vinyl ketone cleanly affords the metallacycle **8**.

**Scheme III**




No evidence for competitive reaction with the olefin moiety, either in a 1,2- or 1,4-manner, was observed. When **2** was heated under an atmosphere of ethylene, metallacycle **10** could be isolated in good yield, demonstrating that isolated olefins are suitable substrates in these metallacycle-forming reactions.

We next examined the possibility of trapping **3** with a donor ligand. Thermolysis of **2** in the presence of several ligands, THF, pyridine, $PMe_3$, and $P(OMe)_3$, was examined by $^1H$ NMR. No products could be observed in the first two cases. However, as in the zirconium case, we were able to observe the $PMe_3$-stabilized complex **1a**. When compound **2** was heated in the presence of a 2-fold excess of trimethylphosphine, **1a** could be isolated in 40–60% yield (eq 2).

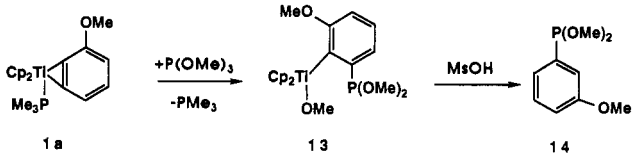



(2)

**2** **1a**

In solution at room temperature, compound **1a** exhibited dynamic NMR behavior ($^1H$, $^{13}C$, $^{31}P$) which we attribute to the reversible dissociation of trimethylphosphine. At lower temperatures the spectra sharpen, showing two sets of signals in a ratio of 1:4. This is consistent with the presence of two isomers, *anti*-**1a** and *syn*-**1a** (Scheme III), with the presumably more stable *anti* isomer predomi-

**Scheme IV**

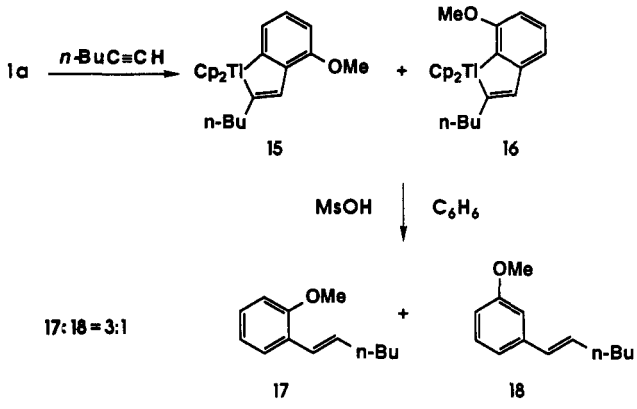



nating.[13] That the isomers are in equilibrium in solution is shown by the coalescence of signals at higher temperatures (i.e., 50 °C for methoxy signals, $^1$H NMR, 300 MHz). Addition of $PMe_3$ to solutions of compound **1a** (10-fold excess) did not change the relative proportion of the isomers. No sharpening of the spectral lines was observed under these conditions. The dissociative equilibrium depicted in Scheme III could explain the effect of added $PMe_3$ upon the reactivity of compound **1a**. For example, when **1a** was heated to 60 °C in the presence of 3-hexyne, metallacycle **4** was formed. In contrast, no reaction was observed when the same experiment was conducted in the presence of a 10-fold excess of trimethylphosphine. This reduced reactivity reflects the decreased availability of the phosphine-free intermediate **3**. This is consistent with the notion that it is the more reactive coordinatively unsaturated intermediate **3** which reacts with the alkyne.

When **2** was thermolyzed in the presence of trimethyl phosphite, the formation of a new compound, **13**, was observed. Reaction of **1a** with $P(OMe)_3$ at room temperature also led to **13** in 84% isolated yield, along with free trimethylphosphine (Scheme IV). Compound **13** displayed three different signals in the methoxy region in both the $^1$H and $^{13}$C NMR spectra. One of the methoxy signals in the proton NMR spectrum of **13** was a doublet ($^3J_{HP}$ = 10.1 Hz) with intensity 6, and the two remaining (one of them corresponding to the aryl-bounded methoxy) were singlets of intensity 3. From this it was deduced that one of the P–O bonds of $P(OMe)_3$ had undergone cleavage, the $P(OMe)_2$ unit becoming attached to the aromatic ring and the methoxy group transferred to the titanium center. Additional support for the proposed structure came from the cleavage of **13** with methanesulfonic acid, which afforded the dimethyl phosphonite **14**. Although the titanium-bound methoxy carbon atom appears as a doublet in the $^{13}$C{$^1$H} NMR spectrum of **13** due to long-range coupling with the phosphorus atom ($J_{CP}$ = 12.7 Hz), additional coordination of the phosphorus atom to titanium seems unlikely, since the $^{31}$P chemical shift in complex **13** (156.4 ppm) is similar to that in compound **14** (160.0 ppm).

The cleavage of a phosphite P–O bond by a transition-metal alkyl is not a common process.[14] The most usual reactivity pattern of transition-metal phosphite complexes is Arbuzov-like reactions, which proceed with initial coordination of the phosphorus atom to the metal, followed by a C–O cleavage to finally yield a species containing a M–P bond.[14a] Presumably, the formation of a Ti–O bond is the driving force for this process. This reaction may proceed by initial coordination of an oxygen atom or by a $\sigma$-bond metathesis mechanism.[15] This transformation can be regarded as being analogous to the reaction of trialkyl phosphites with organolithium or organomagnesium reagents. It should be noted that, in these cases, the lack of control usually leads to mixtures of products $P(OR)_nR'_{3-n}$.[16]

**Scheme V**




The availability of **1a** allowed us to study other reactions that were difficult or impossible to perform by using **3** generated by thermolysis of **2**. While thermolysis of **2** in the presence of internal alkynes cleanly gives the corresponding metallacycles, terminal alkynes such as 1-hexyne afford complex mixtures of compounds, in a nonreproducible fashion. In contrast, **1a** reacts with 1-hexyne to afford a mixture composed mainly of two metallacycles, in an approximate ratio of 1:3 (Scheme V). Acid cleavage of this mixture yields 1-methoxy-2-(1-hexenyl)benzene (**17**) and 1-methoxy-3-(1-hexenyl)benzene (**18**) as the major and minor isomers, respectively (Scheme V). The identity of these olefins has been confirmed by comparison with an authentic sample prepared by an independent procedure.[17a] This is the only case in our study in which the insertion *syn* to the aryl substituent occurs preferentially.[17b] The proportion of the insertion products is similar to the *syn*:*anti* ratio of **1a** found in solution. A possible explanation of this behavior is that the 1-hexyne molecule approaches the titanium center prior to phosphine dissociation (Scheme VI). Such preassociative behavior is well-known in organic chemistry.[18] As in the 3-hexyne case, the reaction rate is dramatically lowered by addition of a 10-fold excess of trimethylphosphine. Thus, although the site of attack by the alkyne molecule is determined by the initial position of the ligand in the complex, phosphine dissociation may be required before the alkyne insertion takes place. This latter result may be due to competitive inhibition by excess phosphine which prevents binding of the alkyne to the titanium center.

Another interesting feature of this reaction is the regioselectivity with respect to the position of the alkyne substituent in the products. In both **15** and **16**, the *n*-butyl group ends up on the carbon atom $\alpha$ to the titanium. This is in contrast to what is observed in the insertion of nitriles (*vide supra*). However, it should be noted that the regioselectivity of the nitrile insertion is undoubtedly controlled by the higher relative affinity of the metal for

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(17) (a) Miyaura, N.; Suzuki, A. *J. Chem. Soc., Chem. Commun.* **1979**, 866. (b) For a related example, cf.: Buchwald, S. L.; Kreutzer, K. A.; Fisher, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 4600.

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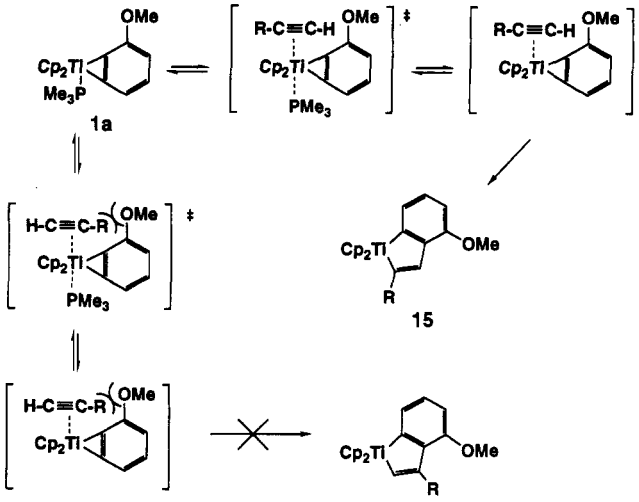
**Scheme VI**




nitrogen,[19] while steric effects should dominate the insertion of alkynes. The final orientation of the substituents in the products of this reaction suggests that those transition states in which the *n*-butyl group of the alkyne is positioned in the wedge between the two Cp groups[20] experience less steric crowding than those in which the *n*-butyl is oriented toward the *ortho* substituents of the benzyne ligand.

## Conclusions

The titanocene complex of 3-methoxybenzyne has been generated by thermolysis of methyl(2-methoxyphenyl)titanocene. This complex can be isolated as its trimethylphosphine adduct **1a** or generated and used in situ. Much of the chemistry of **1a** and **3** parallels that seen for the analogous zirconocene–benzyne complexes. One interesting difference, albeit with some precedent,[7] is that thermally generated **3** reacts cleanly with methyl vinyl ketone to give **8**. Coupling reactions of this type may be of considerable utility in organic synthesis.[23]

## Experimental Section

All manipulations were performed using either standard Schlenk techniques under argon or a Vacuum Atmospheres drybox under $N_2$, unless stated otherwise. Argon used in the Schlenk work was purified by passage through columns of BASF-RS-11 (Chemalog) and Linde 4-Å molecular sieves. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker WM-250, a Varian XL-300, or a Varian XL-500 Fourier transform spectrometer. Infrared (IR) spectra were recorded on a Mattson Cygnus Starlab 100 Fourier transform spectrometer. Only significant IR bands are reported. Electron-impact high-resolution mass determinations (HRMS) were recorded on a Finnegan MAT system 8200 spectrometer. Elemental analyses were performed by Desert Analytics, Tucson, AZ, or Oneida Research Services Inc., Whitesboro, NY. Spinning-plate chromatography was performed with a Harrison Research Chromatotron using 2 mm thick plates coated with Merck Kieselgel 60 PF25A silica gel.

Tetrahydrofuran, benzene, and diethyl ether were dried and deoxygenated by refluxing over sodium/benzophenone ketyl followed by distilling under argon or nitrogen. Hexane was deolefinated by standard procedures and then stored over $CaH_2$. The deolefinated hexane thus obtained was dried and deoxygenated by reflux over sodium/benzophenone ketyl followed by distillation. Toluene was dried over sodium followed by distillation under nitrogen. Dichloromethane was dried by distillation from $CaH_2$ under nitrogen.

**$Cp_2Ti(\eta^2$-1,2-$C_6H_4$-3-OMe)$(PMe)_3$ (1a).** A solution of **2** (7.2 g, 24 mmol) and $PMe_3$ (5 mL, *ca.* 50 mmol) in benzene (30 mL) was heated to 80 °C for 1.5 h, during which time the color of the mixture changed to yellow-green. After cooling and removal of volatiles under vacuum, the residue was extracted with toluene (35 mL) and the extract filtered and cooled to −20 °C for 24 h. The mother liquor was separated from the crystals, which were washed with hexane (3 × 10 mL) until the green color disappeared, leaving 3.5 g of a yellow solid. The mother liquor was concentrated to half of its original volume and cooled again, affording a second crop (1.25 g), which was washed in the same way. Combined yield: 4.75 g, 13.2 mmol, 55%. IR (Nujol mull): 1567.2 m (*ν*(aromatic C=C)) 947.5 m (*ν*(P—C)) $cm^{-1}$. $^1H$ NMR (500 MHz, toluene-$d_8$, −70 °C): *anti*:*syn* isomers in a ratio of 4:1; *anti* isomer δ 1.02 (d, 9H, $J_{HP}$ = 7.3 Hz, $P(CH_3)_3$), 3.87 (s, 3H, $OCH_3$), 4.87 (s, 10H, Cp), 6.84 (d, *J* = 6.8 Hz, 1H, C*H* arom), 7.21 (d, *J* = 5.8 Hz, 1H, C*H* arom), 7.41 (dd, *J* = 6.8, 5.8 Hz, 1H, C*H* arom); *syn* isomer δ 1.39 (d, *J* = 7.8 Hz, 9H, $P(CH_3)_3$), 3.47 (s, 3H, $OCH_3$), 4.87 (s, 10H, Cp), 6.46 (d, *J* = 6.8 Hz, C*H* arom), 7.51 (t, *J* = 6.8 Hz, C*H* arom), 7.58 (d, *J* = 6.8 Hz, 1H, C*H* arom). $^1H$ NMR (300 MHz, $C_6D_6$, 70 °C): δ 1.42 (bs, 9H, $P(CH_3)_3$), 3.79 (bs, 3H, $OCH_3$), 5.00 (s, 10H, Cp), 6.30 (bd, *J* = 6.8 Hz, 1H, C*H* arom), 7.31 (bd, *J* = 6.8 Hz, 1H, C*H* arom), 7.37 (t, *J* = 6.8 Hz, 1H, C*H* arom). $^{13}C\{^1H\}$ NMR (300 MHz, THF-$d_8$, −70 °C): *anti* isomer δ 19.2 (d, $^1J_{CP}$ = 25.7 Hz, $P(CH_3)_3$), 54.8 ($OCH_3$), 103.1 (Cp), 111.9, 124.7, 129.2 (*C*H arom), 149.9 (d, $^2J_{CP}$ = 15.3 Hz, $C_{quat}$ arom), 156.2 (d, $^2J_{CP}$ = 54.7 Hz, $C_{quat}$ arom), 162.6 ($C_{quat}$–$OCH_3$); *syn* isomer δ 19.7 (d, $^1J_{CP}$ = 25 Hz, $P(CH_3)_3$), 54.3 ($OCH_3$), 103.1 (Cp), 106.6, 122.1, 130.2 (*C*H arom), 129.8 (d, $^2J_{CP}$ = 54.7, $C_{quat}$ arom), 167.5 ($C_{quat}$–$OCH_3$), 180.4 (d, $^2J_{CP}$ = 13.9 Hz, $C_{quat}$ arom). $^{31}P\{^1H\}$ NMR (121.5 MHz, $C_6D_6$, 20 °C): *anti* isomer δ 14.8 (bs); *syn* isomer δ 11.8 (bs). Anal. Calcd for $C_{22}H_{25}OPTi$ (crystallized from $Et_2O$): C, 66.67; H, 6.99. Found: C, 66.54; H, 6.78.

**(2-Methoxyphenyl)methyltitanocene (2).** To a solution of 2-bromoanisole (6.20 g, 33.0 mmol) in THF (50 mL) stirred at −80 °C was added dropwise 20 mL of *n*-BuLi (1.6 M in hexane, 32.0 mmol). The mixture was stirred for 15 min at this temperature and then 20 min at −20 °C. The resulting solution was added dropwise to a solution of $Cp_2Ti(Cl)Me$ (7.52 g, 33 mmol) in 250 mL of THF at −80 °C. Once the addition was complete, the solution was allowed to warm to ambient temperature. Stirring was continued for 15 min, and then the solvent was evaporated under reduced pressure, leaving a solid yellow residue. This residue was washed with hexane (2 × 50 mL) and then extracted with 50 mL of benzene, the extract filtered, and the solvent removed. The residue was recrystallized from diethyl ether. Yield: 5.44 g (18.15 mmol, 55%; typically, the yield is in the range 50–70%). $^1H$ NMR (300 MHz, $C_6D_6$, 20 °C): δ 0.5 (s, 3H, Ti–$CH_3$), 3.16 (s, 3H, aryl–$OCH_3$), 5.85 (s, 10H, Cp), 6.38 (dd, *J* = 7.2, 0.9 Hz, 1H, C*H* arom), 6.49 (dd, *J* = 6.5, 1.6 Hz, 1H, C*H* arom), 6.81 (td, *J* = 6.5, 0.9 Hz, 1H, C*H* arom), 7.16 (ddd, *J* = 7.2, 6.5, 1.6 Hz, 1H, C*H* arom). $^{13}C\{^1H\}$ NMR (75 MHz, $C_6D_6$, 20 °C): δ 53.8, 54.1 (Ti–$CH_3$ and O–$CH_3$), 108.4 (*C*H arom), 114.1 (Cp), 121.2, 125.9, 133.3 (*C*H arom), 162.0, 177.6 ($C_{quat}$ arom). Anal. Calcd for $C_{18}H_{20}OTi$: C, 72.00; H, 6.71. Found: C, 71.61; H, 6.69.

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**$Cp_2Ti[C(Et)=C(Et)(2\text{-}C_6H_3)]\text{-}3\text{-}(OMe)$ (4).** A solution of **2** (300 mg, 1.00 mmol) and EtC≡CEt (82 mg, 1.00 mmol) in THF (10 mL) was heated at 85 °C for 2 h. After this time, $^1H$ NMR showed that complete conversion to the metallacycle had occurred. The solution was concentrated to ca. 3–4 mL, and an equal volume of hexane was carefully added. The solution was cooled at −20 °C overnight, during which time crystals had formed. These were isolated by filtration to yield 120 mg (33.7 mmol, 34%, dark green crystals) of **4**. $^1H$ NMR (250 MHz, $C_6D_6$, 20 °C): δ 0.97 (t, $J$ = 7.4 Hz, 3H, $CH_3$), 1.22 (t, $J$ = 7.4 Hz, 3H, $CH_3$), 1.36 (q, 2H, $J$ = 7.4 Hz, $CH_2$), 2.31 (q, 2H, $J$ = 7.4 Hz, $CH_2$), 3.17 (s, 3H, $OCH_3$), 6.02 (s, 10H, Cp), 6.24 (d, $J$ = 8.0 Hz, 1H, C*H* arom), 6.83 (d, $J$ = 7.6 Hz, 1H, C*H* arom), 7.11 (dd, $J$ = 8.0, 7.6 Hz, 1H, C*H* arom). $^{13}C\{^1H\}$ NMR (62.5 MHz, $CDCl_3$, 20 °C): δ 13.8, 14.7 ($CH_3$), 20.9, 25.9 ($CH_2$), 54.2 (O–$CH_3$), 104.0 (*C*H arom), 113.4 (Cp), 125.2 (*C*H arom), 136.2 (*C*H arom), 144.4 ($C_{quat}$ atom or olefin), 159.9 (2$C_{quat}$ arom or olefin), 178.3 ($C_{quat}$ arom or olefin). Anal. Calcd for $C_{23}H_{26}OTi$: C, 75.40; H, 7.06. Found: C, 75.86; H, 7.15.

**Reaction of 4 with $CH_3SO_3H$. (*E*)-3-(3-Methoxyphenyl)-3-hexene (5).** A solution of 300 mg (1.00 mmol) of **4** and 3-hexyne (95 mg, 1.15 mmol) in 10 mL of benzene was heated at 80 °C for 1.5 h. The solution was cooled to room temperature, and methanesulfonic acid (192 mg, 2.00 mmol) in 10 mL of $CH_2Cl_2$ was added dropwise. The color changed from red-green to orange-red. As stirring continued, some red $Cp_2Ti(OMs)_2$ started to precipitate. After 15 min, the solvent was evaporated under reduced pressure, and the red, microcrystalline residue was extracted with diethyl ether (3 × 5 mL). The combined filtrates were evaporated, and the residue was extracted with 3 × 5 mL of pentane. The faint orange solution thus obtained was concentrated, and the product was purified by spinning-plate chromatography (hexane). Yield: 148 mg (0.78 mmol, 78%). $^1H$ NMR (300 MHz, $CDCl_3$, 20 °C): δ 0.93, 1.05 (t, $J$ = 7.7 Hz, 3H, $CH_3$), 2.19 (dq, $J$ = 7.7, 7.3 Hz, 2H, $CH_2CH$=C), 2.48 (q, $J$ = 7.7 Hz, 2H, $CH_2CAr$=C), 3.81 (s, 3H, $OCH_3$), 5.64 (t, $J$ = 7.3 Hz, 1H, $CH_2CH$=C), 6.76 (ddd, $J$ = 7.6, 2.9, 0.7 Hz, 1H, C*H* arom), 6.89 (dd, $J$ = 2.9, 2.1 Hz, 1H, C*H* arom), 6.95 (ddd, $J$ = 7.6, 2.1, 0.7 Hz, 1H, C*H* arom), 7.20 (t, $J$ = 7.6 Hz, 1H, C*H* arom). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 20 °C): δ 145.9, 150.5 ($CH_3$), 21.7, 22.9 ($CH_2$), 55.0 ($OCH_3$), 111.5, 112.2, 118.8, 129.0, 130.0 (*C*H arom and olefin), 140.9, 144.7, 159.5 ($C_{quat}$ arom and olefin). HRMS: calcd for $C_{13}H_{18}O$ 190.1357, found 190.1356 amu.

**$Cp_2Ti[N=C(C_6H_4\text{-}4\text{-}Br)\text{-}2\text{-}C_6H_3]\text{-}3\text{-}(OMe)$ (6).** A solution of **2** (150 mg, 0.50 mmol) and of *p*-bromobenzonitrile (94 mg, 0.52 mmol) in benzene (10 mL) was heated at 80 °C for 1.5 h. After the mixture was cooled to room temperature, the solvent was removed under vacuum and the residue extracted with 30 mL of diethyl ether. The volume was reduced to 6 mL and the solution cooled to −20 °C overnight. Filtration of the dark red crystals which had formed yielded 86 mg of product. Adding 2 mL of hexane to the mother liquor, concentrating to 1 mL, and cooling to −20 °C over 2 days yielded 40 mg more product. Overall yield: 126 mg, 0.27 mmol, 54%. IR (Nujol mull): 1654 m (ν(C=N)) $cm^{-1}$. $^1H$ NMR (300 MHz, $C_6D_6$, 20 °C): δ 3.24 (s, 3H, $OCH_3$), 5.84 (s, 10H, Cp), 6.39 (d, $J$ = 8.0 Hz, 1H, C*H* arom), 6.77 (d, $J$ = 8.0 Hz, 1H, C*H* arom), 7.02 (t, $J$ = 8.0 Hz, 1H, C*H* arom), 7.25 (AA′BB′ system, 4H, *p*-Br$C_6H_4$). $^{13}C\{^1H\}$ NMR (75 MHz, $C_6D_6$, 20 °C): δ 54.5 ($OCH_3$), 108.4 (*C*H arom), 112.3 (Cp), 119.8 (*C*H arom), 122.3 ($C_{quat}$ arom), 126.0 (*C*H arom), 129.9, 131.4 (2*C*H arom, $C_6H_4Br$), 138.3, 158.6, 161.9, 162.6 ($C_{quat}$ arom), 183.4 (*C*=N). Anal. Calcd for $C_{24}H_{20}BrNOTi$: C, 61.82; H, 4.32; N, 3.00. Found: C, 61.57; H, 4.43; N, 2.71.

**Hydrolysis of 6. 4-Bromo-3′-methoxybenzophenone (7).** A solution of **2** (150 mg, 0.50 mmol) and *p*-bromobenzonitrile (96.3 mg, 0.53 mmol) in THF (10 mL) was heated at 80 °C for 1.5 h. The mixture was cooled to room temperature, 1 N HCl (1 mL) was added, and the mixture was stirred for 4 h. The solution was concentrated to approximately half the initial volume and treated with 5 mL of diethyl ether and 1 mL of saturated $NaHCO_3$ solution. The resulting white precipitate and the aqueous phase were removed. The pale yellow organic phase was concentrated, passed through a short silica column, and purified by spinning-plate chromatography to afford 58 mg (0.22 mmol, 44%) of a colorless oil that solidified on standing at −20 °C (mp 47.6–48.6 °C). IR (liquid film): 1654.6 m (ν(CO)) $cm^{-1}$. $^1H$ NMR (500 MHz, $CDCl_3$, 20 °C): δ 3.87 (s, 3H, $OCH_3$), 7.15 (ddd, $J$ = 8.0, 2.7, 1.2 Hz, 1H, C*H* arom), 7.30 (dt, $J$ = 7.6, 1.2 Hz, 1H, C*H* arom), 7.33 (dd, $J$ = 2.7, 1.2 Hz, 1H, C*H* arom), 7.39 (dd, $J$ = 8.0, 7.6 Hz, 1H, C*H* arom), 7.66 (AA′BB′ system, 4H, *p*-$C_6H_4Br$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 20 °C): δ 55.8 ($OCH_3$), 114.6, 119.5, 123.0 (*C*H arom), 127.9 ($C_{quat}$ arom), 129.6 (*C*H arom), 131.9 (4 *C*H arom, *p*-$C_6H_4Br$), 131.9, 136.7, 138.8, 160.0 ($C_{quat}$ arom), 195.7 (*C*O). HRMS: calcd for $C_{14}H_{11}BrO$ 289.9942, found 289.9941 amu.

**$Cp_2Ti[OC(Me)(CH=CH_2)\text{-}2\text{-}C_6H_3]\text{-}3\text{-}(OMe)$ (8).** A solution of **2** (300 mg, 1 mmol) and freshly distilled methyl vinyl ketone (80 mg, 1.10 mmol) in 10 mL of benzene was heated for 1.5 h at 80 °C. After the mixture was cooled to room temperature, the solvent was removed under vacuum and the residue extracted with 20 mL of a 3:1 mixture of hexane and diethyl ether; the extract was filtered, concentrated to a volume of ca. 12 mL, and cooled to −20 °C. Compound **8** slowly crystallized over 3–4 days at this temperature, giving a first crop of orange-red crystals (160 mg). The mother liquor was concentrated to 2 mL and cooled for 2 days more, to afford 105 mg of additional product. Overall yield: 265 mg, 74.9 mmol, 75%. $^1H$ NMR (300 MHz, $C_6D_6$, 20 °C): δ 1.60 (s, 3H, $CH_3$), 3.28 (s, 3H, $OCH_3$), 5.03 (dd, $J$ = 10.7, 2.0 Hz, 1H, *cis*-HC=C*H*H), 5.30 (dd, $J$ = 17.0, 2.0 Hz, 1H, *trans*-HC=CH*H*), 6.08 (s, 5H, Cp), 6.11 (s, 5H, Cp), 6.28 (dd, $J$ = 17.0, 10.7 Hz, 1H, *H*C=CHH), 6.37 (d, $J$ = 7.9 Hz, C*H* arom), 6.47 (d, $J$ = 7.6 Hz, C*H* arom), 7.08 (dd, $J$ = 7.9, 7.6 Hz, C*H* arom). $^{13}C\{^1H\}$ NMR (75 MHz, $C_6D_6$, 20 °C): δ 33.4 ($CH_3$), 45.7 ($OCH_3$), 90.5 ($C_{quat}$), 106.5 (*C*H), 110.5 ($CH_2$=CH), 115.2, 115.3 (diastereotopic Cp's), 118.8, 126.4, 146.3 (*C*H arom), 162.0, 165.8, 174.0 ($C_{quat}$ arom). Anal. Calcd for $C_{21}H_{22}O_2Ti$: C, 71.18; H, 6.26. Found: C, 71.02; H, 6.25.

**Reaction of 8 with Methanesulfonic Acid. 3-(3-Methoxyphenyl)-1-buten-3-ol (9).**[21] A solution of **8** was obtained by heating compound **2** (300 mg, 1.00 mmol) and freshly distilled methyl vinyl ketone (80 mg, 1.10 mmol) in 10 mL of $C_6D_6$ for 1.5 h at 80 °C. The volatile components were removed *in vacuo*, and the residue was redissolved in benzene (10 mL). Methanesulfonic acid (192 mg, 2.00 mmol) in dichloromethane (10 mL) was added at room temperature. The mixture was stirred for 4 h, and the solvent was removed under vacuum. The residue was extracted with hexane (1 × 30 mL, 1 × 10 mL), and the filtered hexane solution was evaporated to leave 110 mg (0.67 mmol, 67%) of **9**. $^1H$ NMR ($CDCl_3$, 20 °C, 300 MHz): δ 3.79 (s, 3H, $OCH_3$), 5.12 (dd, $J$ = 10.7, 1.0 Hz, 1H, *trans*-HC=CH*H*), 5.28 (dd, $J$ = 17.4, 1.0 Hz, 1H, *cis*-HC=C*H*H), 6.14 (dd, $J$ = 17.4, 10.7 Hz, 1H, *H*C=CHH), 6.78 (ddd, $J$ = 7.7, 1.3, 0.8 Hz, 1H, C*H* arom), 7.01 (ddd, $J$ = 7.5, 2.0, 0.8 Hz, 1H, C*H* arom), 7.02 (dd, $J$ = 1.3, 2.0 Hz, 1H, C*H* arom), 7.24 (dd, $J$ = 7.7, 7.5 Hz, 1H, C*H* arom).

**$Cp_2Ti[CH_2CH_2\text{-}2\text{-}C_6H_3]\text{-}3\text{-}OMe$ (10).** A solution of compound **4** (300 mg, 1 mmol) in toluene was heated at 80 °C for 1.5 h under an atmosphere of ethylene (ca. 2 atm). After the reaction mixture was cooled to room temperature, the solvent was evaporated to leave a dark red solid residue. The resulting material was recrystallized from a 1:2 THF–hexane mixture. Yield: 273 mg (0.87 mmol, 87%). $^1H$ NMR (300 MHz, $C_6D_6$, 20 °C): δ 1.49 (t, $J$ = 7.0 Hz, 2H, $CH_2$), 3.14 (s, 3H, $OCH_3$), 3.19 (t, $J$ = 7.0 Hz, 2H, $CH_2$), 6.00 (s, 10H, Cp), 6.24 (d, $J$ = 8.1 Hz, 1H, C*H* arom), 6.60 (d, $J$ = 7.3 Hz, 1H, C*H* arom), 6.99 (dd, $J$ = 8.1, 7.3 Hz, 1H, C*H* arom). $^{13}C\{^1H\}$ NMR (75 MHz, $C_6D_6$, 20 °C): δ 30.0, 53.8 ($CH_2$), 58.9 ($OCH_3$), 105.7 (*C*H arom), 114.7 (Cp), 119.6, 126.5 (*C*H arom), 177.7, 161.3, 148.8 ($C_{quat}$ arom). Anal. Calcd for $C_{19}H_{20}OTi$: C, 73.08; H, 6.46. Found: C, 72.80; H, 6.59.

**Reaction of Compound 10 with Methanesulfonic Acid. 3-Ethylanisole (11).** A solution of **10** in benzene, obtained by heating 731 mg (2.43 mmol) of **2** in 10 mL of $C_6H_6$ at 80 °C for 1.5 h under *ca.* 2 atm of ethylene, was treated with $CH_3SO_3H$

(467 mg, 4.86 mmol) dissolved in 10 mL of $CH_2Cl_2$. The mixture was stirred for 1 h, the solvent was evaporated under reduced pressure, and the residue was extracted with 2 × 30 mL of pentane and 1 × 30 mL of boiling pentane. The solution was concentrated to ca. 1 mL and then eluted through a short $SiO_2$ column with pentane. Evaporation of the pentane left 3-ethylanisole (271 mg, 82%). $^1H$ NMR (300 MHz, $CDCl_3$, 20 °C): δ 1.22 (t, $J$ = 7.6 Hz, 3H, $CH_3CH_2$), 2.62 (q, $J$ = 7.6 Hz, 2H, $CH_3CH_2$), 6.73 (dd, $J$ = 7.6, 7.5 Hz, 1H, C*H* arom), 6.74 (dd, $J$ = 7.6, 7.5 Hz, 1H, C*H* arom), 6.79 (d, $J$ = 7.5 Hz, 1H, C*H* arom), 7.6 (t, $J$ = 7.6 Hz, 1H, C*H* arom).

**$Cp_2Ti(OMe)(1\text{-}C_6H_3\text{-}2\text{-}P(OMe)_2\text{-}5\text{-}(OMe))$ (13).** A solution of benzyne complex **1a** (360 mg, 1 mmol) and a slight excess of trimethyl phosphite (130 mg, 1.04 mmol) in 20 mL of THF was stirred overnight at room temperature. The volatiles were removed *in vacuo*, the yellow residue extracted with 20 mL of diethyl ether, and the extract filtered. The solution was concentrated to 10 mL and cooled to −20 °C overnight, to yield 320 mg (0.84 mmol, 84%) of a yellow solid. The product was recrystallized from a toluene–hexane mixture. IR (Nujol mull): 1016.3 s (ν(P–O)) $cm^{-1}$. $^1H$ NMR (300 MHz, $C_6D_6$, 20 °C): δ 3.31 (s, 3H, $ArOCH_3$), 3.45 (d, $^3J_{HP}$ = 10.1 Hz, 6H, $P(OCH_3)_2$), 4.19 (s, 3H, $Ti\text{–}OCH_3$), 5.88 (s, 10H, Cp), 6.54 (d, $J$ = 7.8 Hz, 1H, C*H* arom), 7.29 (t, $J$ = 7.8 Hz, 1H, C*H* arom), 8.01 (d, $J$ = 7.8 Hz, 1H, C*H* arom). $^{13}C\{^1H\}$ NMR (75 MHz, $C_6D_6$, 20 °C): δ 51.6 (d, $^2J_{CP}$ = 10.7 Hz, $P(OCH_3)_2$), 53.7 ($ArOCH_3$), 67.2 (d, $J_{CP}$ = 12.7 Hz, $TiOCH_3$), 109.5 (*C*H arom), 112.9 (Cp), 124.4 (d, $J_{CP}$ = 6.8 Hz, *C*H arom), 125.2 (*C*H arom), 146.6 (d, $^1J_{CP}$ = 28.3 Hz, $C_{quat}$–P), 162.8 (d, $^2J_{CP}$ = 13.6 Hz, $C_{quat}$–OMe), 174.1 (d, $^2J_{CP}$ = 54.7 Hz, $C_{quat}$–Ti). $^{31}P\{^1H\}$ NMR (121.5 MHz, $C_6D_6$, 20 °C): δ 156.4. Anal. Calcd for $C_{20}H_{25}O_4PTi$: C, 58.82; H, 6.12. Found: C, 59.12; H, 6.23.

**Reaction of Compound 13 with Methanesulfonic Acid. Dimethyl (3-Methoxyphenyl)phosphonite (14).** A solution of 1.02 g (2.8 mmol) of **13** and trimethyl phosphite (353 mg, 2.8 mmol) in THF (40 mL) was stirred overnight at room temperature. The solvent was removed and the residue redissolved in dichloromethane (20 mL). After the mixture was cooled to −55 °C, methanesulfonic acid (528 mg, 5.5 mmol) dissolved in dichloromethane (5 mL) was added dropwise to the resulting suspension. The cooling bath was removed, and when the temperature reached 0 °C, the solvent was evaporated under vacuum. (Note: a longer reaction time allows the product to react with methanol in the presence of traces of acid, resulting in the formation of variable amounts of *m*-$MeOC_6H_4P(O)(H)OMe$ as a byproduct.) The oily residue was redissolved in dichloromethane (20 mL), and toluene (10 mL) was added. The solvent was slowly evaporated, to allow the crystallization of titanocene bis(methanesulfonate). The residue was extracted with hexane (25 mL) and boiling hexane (25 mL). The $Cp_2Ti(OMs)_2$ precipitate was separated by filtration and the hexane evaporated under reduced pressure. The resulting oil was purified by spinning-plate chromatography (hexane–diethyl ether–triethylamine 8:1:1). IR (liquid film): 1041 s, 1012 s (ν(P–O–C)) $cm^{-1}$. $^1H$ NMR ($C_6D_6$, 500 MHz, 20 °C, connectivities established by COSY): δ 3.30 (s, 3H, $Ar\text{–}OCH_3$), 3.32 (d, $^3J_{HP}$ = 10.5 Hz, 6H, $P\text{–}OCH_3$), 6.81 (dm, $J$ = 7.9 Hz, 1H, C*H* arom (H4)), 7.14 (ddm, $J$ = 7.9, 6.5 Hz, 1H, C*H* arom (H5)), 7.31 (m, 1H, C*H* arom (H6)), 7.37 (dm, $^3J_{HP}$ = 5.5 Hz, 1H, C*H* arom (H2)). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 20 °C): δ 52.8 (d, $^3J_{HP}$ = 8.9 Hz, $P(OCH_3)_2$), 54.9 ($ArOCH_3$), 114.1 (d, $J_{CP}$ = 20.2 Hz, *C*H arom), 115.7 (*C*H arom), 121.7 (d, $J_{CP}$ = 21.9 Hz, *C*H arom), 129.1 (d, $J_{CP}$ = 6.2 Hz, *C*H arom), 141.6 (d, $^1J_{CP}$ = 21.8 Hz, $C_{quat}$–P), 159.2 (d, $^2J_{CP}$ = 5.8 Hz, $C_{quat}$–OMe). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 20 °C): δ 160.0 (s). HRMS: calcd for $C_9H_{13}O_3P$ 200.0602, found 200.0603 amu.

**Reaction of Compound 1a with 1-Hexyne. 2-((*E*)-1-Hexen-1-yl)anisole[16] (17) and 3-((*E*)-1-Hexen-1-yl)anisole (18).[22]** A 390-mg (1.08-mmol) amount of **1a**, dissolved in THF (15 mL), was stirred with 1-hexyne (90 mg, 1.1 mmol) for 3 h at room temperature. The solution was evaporated and the residue redissolved in $C_6H_6$ (1 mL). At this point, $^1H$ NMR showed the mixture to contain mainly two metallacyclic species in a 3:1 ratio. The overall spectroscopic yield was nearly quantitative, as estimated by use of ferrocene as internal standard. $CH_3SO_3H$ (206 mg, 2.16 mmol), dissolved in methylene chloride (5 mL), was added dropwise, and stirring was continued for 1 h. The solvent was removed under vacuum and the solid residue extracted with 2 × 20 mL of hexane. GC analysis of this solution showed two olefins in a ratio of 3.2:1. Purification by circular chromatography yielded **17** (12.5 mg, 6.1%) and **18** (10.2 mg, 5%). GC of the isolated compounds confirmed their presence in the crude reaction mixture.

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