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Early-Transition-Metal Ketenimine Complexes: Synthesis, Reactivity, and Structure of Ketenimine-Containing Titanocene and Zirconocene Complexes

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Reaction of $Cp_2M(PMe_3)_2$ complexes (M = Ti, Zr; Cp = η^5-C_5H_5) with the *N*-(*p*-tolyl)-diphenylketenimine Ph′N=C=CPh_2 (Ph′ = *p*-MeC_6H_4) in a 1:1 molar ratio affords the ketenimine-containing metallocene derivatives $Cp_2M(\eta^2$-(*C,N*)-Ph′N=C=$CPh_2)(PMe_3)$ (M = Ti (**1**); Zr (**2**)). The ketenimine ligand reacts in the same way with the "Cp^*_2M" species (Cp* = η^5-C_5Me_5) generated from the reduction of the corresponding $Cp^*_2MCl_2$ complexes with Li^{t}Bu (1:2 molar ratio) to give the related complexes $Cp^*_2M(\eta^2$-(*C,N*)-Ph′N=C=CPh_2) (M = Ti (**3**); Zr (**4**)). The molecular structure of **3** shows a titanium atom bonded to two η^5-cyclopentadienyl rings and a η^2 -(*C,N*)-bonded ketenimine ligand. Reaction of "Cp^*_2Ti" with the ketenimine ligand in a 1:2 molar ratio gives 1,1,5,5-tetraphenyl-3-(*p*-tolyl)-2-(*p*-toluidino)-3-aza-1,4-pentadiene, which probably results from the coupling, followed by hydrolysis, of two ketenimine molecules coordinated to one titanocene moiety. Protonation of **3** with Et_3NHCl or H_2O (1:1 molar ratio) affords the intermediate species $Cp^*_2Ti(X)(\eta^2$-(*C,N*)-Ph′N⩦C(H)⩦CPh_2) (X = Cl (**5**); OH (**6**)), which on hydrolysis evolves to give the enamine Ph′N(H)−CH=CPh_2 as the final product. Finally, **3** reacts reversibly with H_2 to give the hydride enamidate complex $Cp^*_2Ti(H)(\eta^1$-Ph′N−CH=CPh_2) (**7**). The structures of the different compounds have been determined by IR and NMR spectroscopic methods.

Introduction

Ketenes, ketenimines, and related heterocumulenes are very reactive organic molecules whose organic chemistry is now well defined. Several reviews on aspects of their synthesis and reactivity are available.[1] In particular, ketenimine complexes of transition metals have proven to be useful in new synthetic approaches to carbocyclic and four-, five-, and six-membered N-heterocyclic rings.[2] Ketenimine complexes have been commonly prepared by C−C coupling reactions, for example by reacting carbene or carbyne[3] complexes with isocyanides, but only in a few cases have they been prepared directly by coordination of free ketenimines.[4] A family of neutral and cationic ketenimine niobocene complexes $Cp'_2Nb(X)(\eta^2$-(*C,N*)-R′N=C=CPhR) (Cp′ = η^5-$C_5H_4SiMe_3$; X = Cl, Br; R = Me, Et, Ph; R′ = C_6H_5, *p*-BrC_6H_4, *p*-MeC_6H_4) and $[Cp'_2Nb(\eta^2$-(*C,N*)-PhN=C=CPhR)(L)$]^+$ (L = nitriles or isonitriles), prepared using this method, has been described.[5] The results obtained encouraged us to try to prepare analogous ketenimine complexes of group 4 metallocenes, with the aim of further studying their reactivity. In order to explore this chemistry, it was decided to study the reactivity of Ti(II) and Zr(II) complexes $Cp_2M(PM_3)_2$ and Cp^*_2M (Cp = η^5-C_5H_5; Cp* = η^5-C_5Me_5) toward the free *N*-(*p*-tolyl)-diphenylketenimine which had already been succesfully employed in the synthesis of the niobocene complexes. This paper will focus on the synthesis and structural details of new titanium and zirconium ketenimine complexes $Cp_2M(\eta^2$-(*C,N*)-Ph′N=C=$CPh_2)(PMe_3)$ and $Cp^*_2M(\eta^2$-(*C,N*)-Ph′N=C=CPh_2) and some of their transformations.

Results and Discussion

Complexes $Cp_2M(PMe_3)_2$ (M = Ti, Zr) reacted with 1 equiv of *N*-(*p*-tolyl)diphenylketenimine (Ph′N=C=CPh_2,

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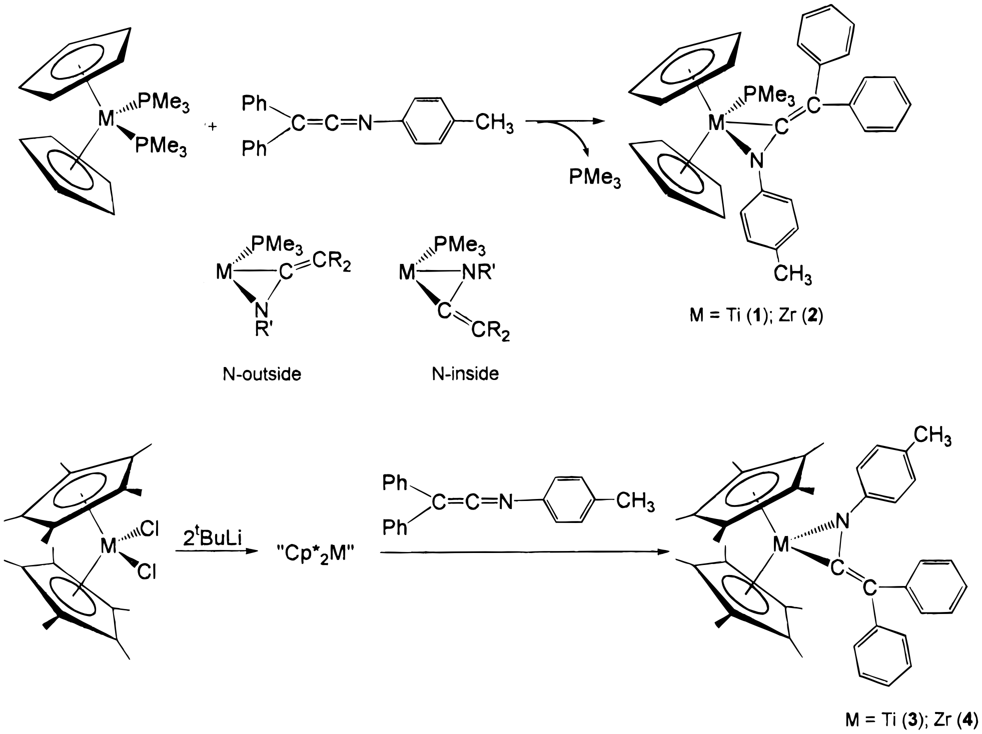
Scheme 1



Ph′ = p-MeC$_6$H$_4$) to give the ketenimine-containing metallocene complexes **1** and **2** (Scheme 1), which were isolated as very air-sensitive pure crystalline solids after appropriate workup (see Experimental Section).

Ketenimine-containing titanocene or zirconocene complexes **3** and **4** were alternatively prepared by reacting the unsaturated moieties "Cp*$_2$M" (prepared "in situ" by reacting the corresponding Cp*$_2$MCl$_2$ species with 2 equiv of Li^{t}Bu) with 1 equiv of the already-mentioned free ketenimine (Scheme 1). These complexes were also isolated as very air-sensitive materials, although **4** was invariably contaminated with 5–10% of organic impurities. Interestingly, when the reaction was carried out in the presence of an excess of PMe$_3$, **4** was isolated as a pure PMe$_3$-free complex. The stabilization of the 16-electron complexes **3** and **4**, even in the presence of PMe$_3$, may be explained by the presence of the Cp* ligand, which is more bulky and electron-donating than the Cp ligand. The new families of ketenimine-containing complexes were characterized by spectroscopic methods. The IR spectra show a band at ca. 1500 cm^{-1}, which agrees with the bathochromic shift reported for other side-on π-bonded ketenimine complexes.[2,5] On the basis of these data, both η^2-(C,N) and η^2-(C,C) coordination modes are possible, and it is only through an X-ray crystal structure determination on **3** that the η^2-(C,N) coordination mode was confirmed. A similar structural situation has previously been found for ketenimine niobocene complexes.[5] A view of **3** is shown in Figure 1, together with the atomic numbering scheme. Selected bond distances and angles are given in Table 1.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 3[a]

Ti–C1	2.431(6)	Ti–C18	2.119(9)
Ti–C2	2.429(6)	Ti–CE1	2.124(7)
Ti–C3	2.422(7)	C18–C19	1.360(12)
Ti–C4	2.439(7)	C19–C20	1.454(13)
Ti–C5	2.416(7)	C19–C26	1.485(10)
Ti–N1	2.024(7)	N1–C18	1.334(13)
CE1–Ti–CE1′	139.6(2)	C11–N1–C18	138.2(9)
C18–Ti–CE1′	106.5(3)	Ti–C18–N1	67.4(5)
C18–Ti–CE1	113.4(3)	N1–C18–C19	139.7(10)
N1–Ti–CE1′	105.9(3)	Ti–C18–C19	152.8(7)
N1–Ti–CE1	109.3(3)	C18–C19–C26	121.3(7)
N1–Ti–C18	37.5(3)	C18–C19–C20	124.1(9)
Ti–N1–C18	75.1(5)	C20–C19–C26	114.7(8)
Ti–N1–C11	144.8(6)		

[a] CE1 is the centroid of the Cp* ring. Prime indicates $-x$, y, $^1/_2 - z$.

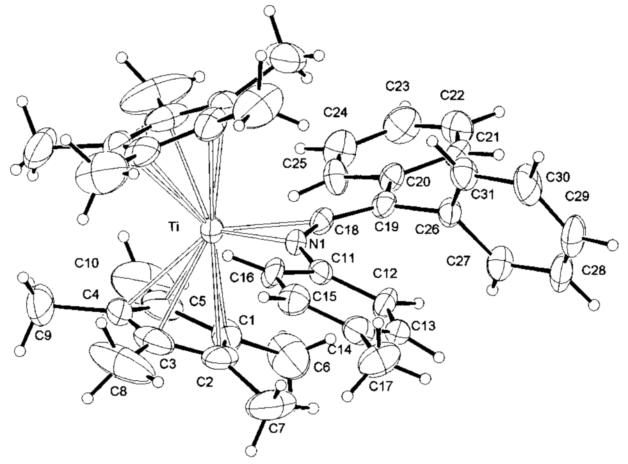
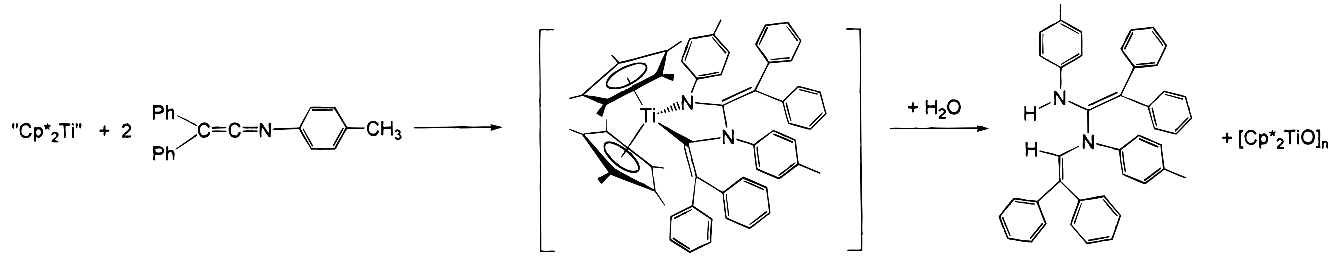


Figure 1. View of **3** with the atomic numbering scheme (30% probability ellipsoids).

The coordination of Ti can be described as a distorted tetrahedron with the vertices occupied by two Cp* ring centroids and by N1 and C18 atoms from the C=N moiety of the ketenimine ligand. The coordination presents a crystallographic C_2 symmetry, with the two-fold axis passing through the Ti atoms and approximately through the C=N midpoint. The element of symmetry generates two disordered ketenimine molecules distributed in two positions of equal occupancy

Scheme 2



factor. Figure 1 shows one of the two molecules. The ketenimine moiety is coordinated as η^2-(*C*,*N*), like that found in three parent complexes[5,6] which were retrieved from the Cambridge Structural Database System files.[7] The coordinating metals in these complexes, however, are cobalt and niobium. The bond distances and angles of the C11−N1=C18=C19 fragment of the ketenimine molecule (N1−C18 = 1.33(1) Å, C18−C19 = 1.36(1) Å, C11−N1−C18 = 138.2(9)°, N1−C18−C19 = 139.7(10)°), despite the high disorder in the Cp* ring, are in accordance with those found in the literature;[5] the moiety is not planar and shows a torsion angle of −16(2)°, probably due to the steric hindrance of the substituents (Ph rings). The two bent Cp* rings form a dihedral angle of 39.9(3)° and are bound to the Ti atom in a symmetric conventional η^5-fashion (Ti−C_{Cp}* ranges, 2.416(7)−2.439(7) Å). To the best of our knowledge, this titanium ketenimine complex is the first to be structurally characterized. The ^{1}H NMR spectra show resonances corresponding to the cyclopentadienyl, the ketenimine, and the phosphine (for **1** and **2**) ligands. The NMR spectra of the crude products isolated before crystallization (see Experimental Section) show the resonances which correspond to only one isomer, the commented η^2-(*C*,*N*) ketenimine-containing isomer, and the results indicate that the possibility that both isomers η^2-(*C*,*N*) and η^2-(*C*,*C*) shoud be formed and the η^2-(*C*,*C*) isomer shoud be simply removed on the crystallization process can be eliminated. Particularly significant are the observed ^{13}C NMR resonances of the coordinated ketenimine, which are shifted when compared to those of the free ketenimine.[8] It is noteworthy that the chemical shift of the ketenimine C_α in **3** appears at lower field than that in the free ketenimine. We are considering the possibility of a different coordination mode (possibly η^2-(*C*,*C*)) for the ketenimine in solution. Furthermore, both ^{1}H and ^{13}C NMR data for **1** and **2** indicate the presence of only one of the two possible N-outside and N-inside isomers (Scheme 1). The N-outside structure is proposed by NOE experiments. In fact, irradiation of the *N*-(*p*-tolyl)ketenimine signal (2.03 and 2.09 ppm for **1** and **2**, respectively) resulted in no observable enhancement of the signal due to the PMe_3 methyl groups.

An interesting reaction was observed when "Cp*₂Ti" was treated with 2 equiv of ketenimine. This reaction, which probably proceeds via the coordination of two ketenimine molecules, followed by coupling and hydrolysis, gives 1,1,5,5-tetraphenyl-3-(*p*-tolyl)-2-(*p*-toluidino)-3-aza-1,4-pentadiene (Scheme 2).

Similar coupling has been observed for ketenes with titanium[9] and niobium[10] organometallics. The new organic compound was isolated as a white, air-sensitive crystalline solid which was characterized spectroscopically.

Finally, the reactivity of **3** toward protonation and hydrogenation processes was considered. **3** reacts with 1 equiv of Et_3NHCl or H_2O to give a new enamine, *N*-(2,2-diphenylvinyl)-4-methylaniline and $[Cp^*{}_2TiO]_n$ or $Cp^*{}_2TiCl_2$ (Scheme 3). However, when the reaction time was short, a mixture of the enamine and the corresponding azatitanacyclobutenes **5** and **6** was isolated.[11]

All attempts to prepare **5** or **6** as pure materials were unsuccessful since they were always contaminated with the enamine. In light of these results, we might suppose that complexes **5** and **6** are formed either by initial protonation at C_α of the complexed ketenimine to give an azatitanacyclobutene, followed by chloride or hydroxide trapping, or by the reverse procedure. However, an alternative process implicating coordination of the Et_3NHCl or H_2O with subsequent proton transfer cannot be excluded. A similar behavior was previously observed for cationic ketenimine-containing niobocene complexes $[Cp'_2Nb(\eta^2\text{-}(C,N)\text{-}PhRCCNPh(L))][X]$,[5b] although in these and related neutral ketenimine-containing niobocene complexes, $[Cp'_2Nb(X)(\eta^2\text{-}(C,N)\text{-}PhRCCNPh)]$,[12] electrophilic attack occurred at the free terminus of the complexed ketenimine ligand to give stable η^2-iminoacyl derivatives. Complexes **5** and **6** and the enamine derivative, which was isolated as a pure, air-sensitive white crystalline solid, have been spectroscopically characterized. The ^{1}H NMR spectra of **5** and **6** show single resonances at 8.28 and 9.38 ppm, respectively, which correspond to the CH group of the azatitanacyclobutene moiety. In addition, a broad resonance at 5.85 ppm for the OH group attached to the Ti center appears for **6**. In the ^{13}C NMR spectrum of **6**, the expected resonances for the azatitanacyclobutene moiety were found at 108.5 (Ph_2C) and 114.3 ppm (CH=N).

Complex **3** also reacts with dihydrogen (1 atm, 25 °C) to give a hydride enamidate complex (**7**), which results

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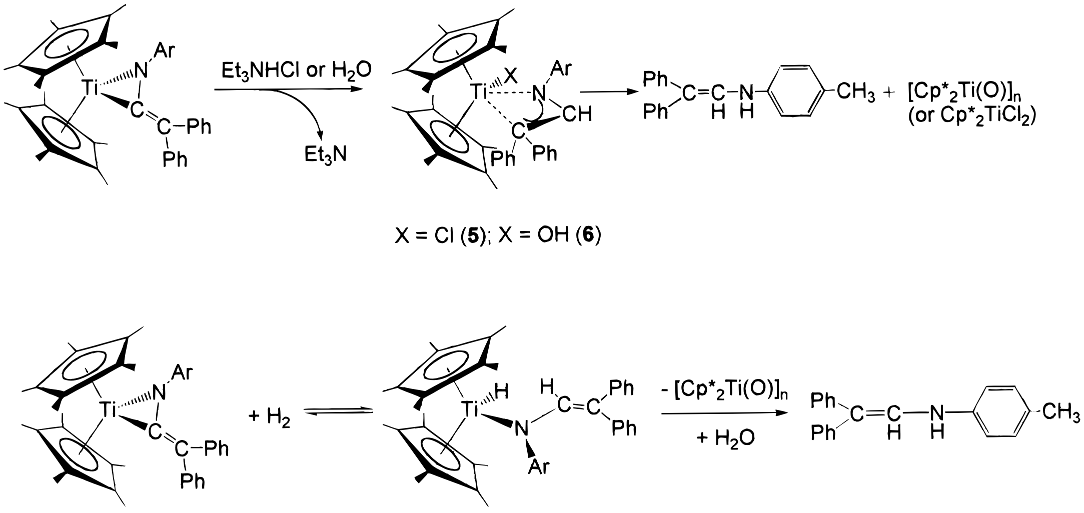
Scheme 3



X = Cl (**5**); X = OH (**6**)

7

from hydrogenolysis of a Ti−C bond (Scheme 3). Complex **7** was spectroscopically characterized when the reaction was monitored by ^{1}H NMR. However, all attempts to isolate **7** working to preparative scale were unsuccessful, because the green reaction solution of **7** was observed to reverse to the initial red solution of **3** on removing the H_2 atmosphere, suggesting that the reaction of the rupture of the azatitanacyclopropane under H_2 atmosphere is highly reversible. This behavior is surprising and unique since analogous ketene-containing zirconocene species described by Bercaw et al.[13] undergo nonreversible hydrogenation processes. In addition, a solution of **7** under H_2 atmosphere was easily hydrolyzed to give the enamine *N*-(2,2-diphenylvinyl)-4-methylaniline. The ^{1}H NMR spectrum of **7** exhibits a broad resonance at 5.50 ppm for the hydride ligand, as well as a resonance at 4.97 ppm for the C*H*-N proton. Different types of unsaturated molecules, such as alkenes, alkynes, aldehydes, ketones, and nitriles, did not react with **1, 2, 3,** or **4** under various experimental conditions, and the reactions with bulky isonitriles, such as 2,6-dimethylphenyl and *tert*-butylisonitrile, gave intractable mixtures of products.

Concluding Remarks

This study has revealed that ketenimine-containing group 4 metallocenes can be prepared by reacting Ti(II) and Zr(II) species with the appropriate free ketenimine. Cp-ring-containing metallocenes are stabilized in the presence of a PMe_3 ligand, while the corresponding Cp*-containing complexes are isolated as the 16-electron species $Cp^*_2M(\eta^2\text{-}(C,N)\text{-}Ph'N{=}C{=}CPh_2)$. C−C coupling of two ketenimine molecules to the titanium coordination sphere has also been observed, and the reactivity of the coordinated ketenimine in the complex $Cp^*_2Ti(\eta^2\text{-}(C,N)\text{-}Ph'N{=}C{=}CPh_2)$ toward H^+ and H_2 was also considered. We believe that the results reported offer a significant advance in the chemistry of cumulene containing early transition metallocenes, and work in this field is ongoing.

Experimental Section

General Considerations. $Ph'N{=}C{=}CPh_2$,[14] $Cp_2Ti(PMe_3)_2$,[15] $Cp_2Zr(PMe_3)_2$,[16] $Cp_2{}^*TiCl_2$,[17] and $Cp_2{}^*ZrCl_2$[18] were prepared by published methods. Li^{t}Bu, Cp_2TiCl_2, and Cp_2ZrCl_2 were used as received from Aldrich.

All reactions and product manipulations were carried out under an inert atmosphere (nitrogen) using standard Schlenk and drybox techniques. Solvents were freshly distilled from appropriate drying agents and degassed before use. Elemental analyses were performed with a Perkin Elmer 2400 microanalyzer. NMR spectra were recorded on a Varian Unity FT-300 instrument. Trace amounts of protonated solvents were used as references, and chemical shifts are reported in ppm relative to SiM_4. IR spectra were recorded as Nujol mulls between CsI plates (in the region 4000−200 cm^{-1}) on a Perkin Elmer PE 833 spectrophotometer.

$Cp_2Ti(\eta^2\text{-}(C,N)\text{-}Ph'N{=}C{=}CPh_2)(PMe_3)$ (1). $Ph'N{=}C{=}CPh_2$ (340 mg, 1.20 mmol) was added to a solution of $Cp_2Ti(PMe_3)_2$ (350 mg, 1.20 mmol) in 25 mL of THF, and this mixture was stirred at room temperature overnight. The solvent and the liberated PMe_3 were removed under vacuum, and the resulting oily brown solid was washed with pentane to give a brown-reddish solid. The crude solid was crystallized by dissolving in THF and placing a layer of pentane above it in a Schlenk tube, and deep red crystals were obtained (89%).

IR (Nujol mull): ν(N=C=C) 1543 cm^{-1}. ^{1}H NMR (C_6D_6): δ 0.59 (s, 9H, PMe_3), 2.03 (s, 3H, *p-Me*C_6H_4), 5.44 (s, 10H, C_5H_5), 6.07 (psd, 2H, J_{HH} = 8.10 Hz), 6.62 (psd, 2H, J_{HH} = 8.10 Hz), 6.80−7.52 (mc, 10H) (phenyl groups). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 20.8 (*p-Me*C_6H_4), 24.7 (PMe_3, J_{PC} = 2.4 Hz), 107.5 (C_5H_5), 128.0 (*C*Ph_2), 146.9 (*C*=N), 120.7, 120.8, 123.5, 123.6, 124.4, 124.5, 127.6, 127.7, 127.8, 127.9, 128.7, 128.8, 132.1, 132.2 (C phenyl groups), 128.9, 129.6, 130.6, 144.9 (C_{ipso} of phenyl groups). Anal. Calcd for $C_{34}H_{36}NPTi$: C, 75.97; H, 6.75; N, 2.61. Found: C, 75.85; H, 6.31; N, 2.50.

$Cp_2Zr(\eta^2\text{-}(C,N)\text{-}Ph'N{=}C{=}CPh_2)(PMe_3)$ (2). This compound was obtained as a red-orange crystalline solid (57%) following the same procedure as described for **1**. It was

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alternatively prepared by the following method: 1.7 mL of Li^{n}Bu (1.6 M in hexane) was added to a solution of Cp_2ZrCl_2 (470 mg, 1.30 mmol) in 25 mL of THF at −78 °C. The reaction mixture was stirred and warmed to room temperature for 15 min, and to the resulting solution was added PMe_3 (3.90 mmol) at −78 °C. Finally, the ketenimine (370 mg, 1.30 mmol) was added to the reaction mixture, which was then stirred for 1 h at room temperature. The solvent and the excess of PMe_3 were removed under vacuum, and the resulting oily reddish solid was washed with pentane to give a red-orange solid, which was crystallized following the method described for **1** (54%).

IR (Nujol mull): ν(N═C═C) 1500 cm^{-1}. ^{1}H NMR (C_6D_6): δ 0.53 (d, 9H, J_{PH} = 6.41 Hz, PMe_3), 2.09 (s, 3H, *p-Me*C_6H_4), 5.59 (s, 10H, C_5H_5), 6.17 (psd, 2H, J_{HH} = 8.10 Hz), 6.60 (psd, 2H, J_{HH} = 8.10 Hz), 7.05−7.84 (mc, 10H) (phenyl groups). ^{13}C{^{1}H} NMR (C_6D_6): δ 14.9 (PMe_3, J_{PC} = 16Hz), 20.9 (*p-Me*C_6H_4), 105.6 (C_5H_5), 105.7 (*C*Ph_2), 170.3 (*C*═N), 120.2, 120.3, 123.3, 123.4, 124.0, 124.1, 127.4, 127.5, 127.8, 127.8, 127.9, 128.0, 132.6, 132.7 (C phenyl groups), 129.9, 144.9, 147.8, 153.4 (C_{ipso} of phenyl groups). Anal. Calcd for $C_{34}H_{36}NPZr$: C, 70.30; H, 6.25; N, 2.41. Found: C, 70.15; H, 6.15; N, 2.37.

Cp*$_2$Ti(η^2-(*C,N*)-Ph′N═C═CPh$_2$) (3). To a suspension of Cp_2TiCl_2 (580 mg, 1.50 mmol) in 25 mL of THF was added Li^{t}Bu (1.7mL, 3.00 mmol, 1.7 M in hexane). After 25 min of stirring at room temperature, the reaction mixture was cooled to −78 °C, and the ketenimine (420 mg, 1.50 mmol) was added. The solution was stirred and slowly warmed to room temperature for 10 min. The solvent was then removed, and the resulting red oily solid was crystallized as deep red crystals by dissolving in THF and placing a layer of pentane above it in a Schlenk tube (54%).

IR (Nujol mull): ν(N═C═C) 1527 cm^{-1}. ^{1}H NMR (C_6D_6): δ 1.73 (s, 30H, C_5Me_5), 2.03 (s, 3H, *p-Me*C_6H_4), 5.79 (psd, 2H, J_{HH} = 8.50 Hz), 6.58 (psd, 2H, J_{HH} = 8.50 Hz), 6.92−7.56 (mc, 10H) (phenyl groups). ^{13}C{^{1}H}NMR (C_6D_6): δ 12.6 (C_5*Me*$_5$), 20.7 (*p-Me*C_6H_4), 102.1 (*C*Ph_2), 124.9 (*C*$_5Me_5$), 120.7, 120.9, 121.9, 122.0 124.6, 124.8, 125.0, 125.2, 127.9, 128.0, 128.1, 128.3, 129.0, 132.2 (C phenyl groups), 127.8, 143.5, 145.1, 146.0 (C_{ipso} of phenyl groups), 200.8 (*C*═N). Anal. Calcd for $C_{41}H_{47}TiN$: C, 81.84; H, 7.87; N, 2.33. Found: C, 81.70; H, 7.60; N, 2.30.

Cp*$_2$Zr(η^2-(*C,N*)-Ph′N═C═CPh$_2$) (4). Method A. The complex was isolated as red crystals contaminated with unidentified impurities in a manner similar to that for **3**.

Method B. To a suspension of Cp*$_2$ZrCl$_2$ (640 mg, 1.50 mmol) in 25 mL of THF was added Li^{t}Bu (1.70 mL, 1.7 M in hexane). After 15 min of stirring at room temperature, PMe_3 (6.00 mmol) and ketenimine (420 mg, 1.50 mmol) were added, and the resulting solution was stirred again for 3 h. Both the solvent and PMe_3 were then removed, and the residue was extracted with 5 mL of toluene to give a solution from which an oily red solid was isolated. After crystallization as **3**, pure red crystals of **4** were obtained (23%).

IR (Nujol mull): ν(N═C═C) 1547 cm^{-1}. ^{1}H NMR (C_6D_6): δ 1.76 (s, 30H, C_5Me_5), 2.08 (s, 3H, *p-Me*C_6H_4), 6.62 (psd, 2H, J_{HH} = 8.50 Hz), 6.76 (psd, 2H, J_{HH} = 8.50 Hz), 5.71−7.51 (mc, 10H) (phenyl groups). ^{13}C{^{1}H} NMR (C_6D_6): δ 11.4 (C_5*Me*$_5$), 20.9 (*p-Me*C_6H_4), 111.4 (*C*Ph_2), 121.2 (*C*$_5Me_5$), 124.0, 124.1, 124.7, 125.2, 126.9, 127.1, 127.4, 127.8, 128.1, 128.5, 130.4, 130.7, 136.0, 136.2 (C phenyl groups), 128.8, 139.2, 141.5, 147.6 (C_{ipso} of phenyl groups), 147.8 (*C*═N). Anal. Calcd for $C_{41}H_{47}ZrN$: C, 76.34; H, 7.34; N, 2.17. Found: C, 76.28; H, 7.15; N, 2.08.

Reaction of “Cp*$_2$Ti” with Ph′N═C═CPh$_2$ (1:2 Molar Ratio). Synthesis of 1,1,5,5-Tetraphenyl-3-(*p*-tolyl)-2-(*p*-toluidino)-3-aza-1,4-pentadiene. To a suspension of Cp*$_2$TiCl$_2$ (330 mg, 0.85 mmol) in 25 mL of THF was added Li^{t}Bu (1mL, 1.70 mmol, 1.7 M in hexane). After 20 min of stirring at room temperature, the reaction mixture was cooled at −78 °C, and the ketenimine (480 mg, 1.70 mmol) was added. The resulting solution was stirred and warmed to room temperature for 20 min H_2O (30 μL) was added afterward to the reaction mixture, which was then stirred for 1 h. The solvent was then removed, and the resulting red oil was extracted (×3) with toluene. A white oily solid was obtained by evaporation of the solvent, which was washed with pentane to afford a white solid (21%).

IR (Nujol mull): 3397 cm^{-1} (m, ν_{N-H}). ^{1}H NMR (C_6D_6): δ 1.89 (s, 3H, *p-Me*C_6H_4), 2.00 (s, 3H, *p-Me*C_6H_4), 4.48 (s, 1H, NH), 5.93 (s, 1H, C═CH), 6.30 (2H), 6.60 (2H), 6.70−7.30 (mc, 24H) (phenyl groups). ^{13}C{^{1}H} NMR (C_6D_6): δ 20.5, 20.5 (*p-Me*C_6H_4), 115.5, 119.3 (Ph_2*C*), 125.5, 126.3, 127.2, 127.2, 127.5, 127.5, 127.8, 128.1, 128.3, 128.5, 128.6, 128.7, 128.8, 129.1, 129.3, 129.5, 129.7, 130.1, 130.2, 130.3, 130.4, 130.5, 131.2, 131.3, 131.4, 131.5, 131.7, 131.8, 131.9, 132.0 (C phenyl and vinyl groups), 129.9, 129.9, 139.9, 140.5, 141.1, 142.1, 143.9, 144.2 (C_{ipso} of phenyl groups). Anal. Calcd for $C_{42}H_{36}N_2$: C, 88.69; H.6.38; N, 4.92. Found: C, 89.48; H. 6.74; N, 4.59.

Reactions of 3 with Et$_3$NHCl or H$_2$O. To a mixture of **3** (330 mg, 0.55 mmol) and Et_3NHCl (70mg, 0.55 mmol) was added 10 mL of THF. The solution was stirred overnight, and then the solvent was removed in vacuo, and the resulting residue was extracted with pentane (2 × 10 mL). The solution was concentrated to 2 mL, and after cooling to −30 °C a white solid of *N*-(2,2-diphenylvinyl)-4-methylaniline was obtained (46%). A similar procedure with H_2O was used.

IR (Nujol mull): 3413 cm^{-1} (m, ν_{N-H}). ^{1}H NMR (C_6D_6): δ 2.06 (s, 3H, *p-Me*C_6H_4), 5.91 (1H, NH), 6.20 (2H), 6.80 (2H), 7.02−7.29 (mc, 11H) (phenyl and vinyl groups). ^{13}C{^{1}H} NMR (C_6D_6): δ 20.5 (*p-Me*C_6H_4), 117.4 (Ph_2*C*), 114.3, 115.0, 125.6, 125.7, 125.9, 126.7, 127.1, 127.5, 128.6, 129.0, 129.5, 130.1, 130.3, 130.6, 130.8 (C phenyl and vinyl groups), 129.2, 139.4, 140.7, 142.5 (C_{ipso} phenyl groups). Anal. Calcd for $C_{21}H_{19}N$: C, 88.38; H, 6.71; N, 4.91. Found: C, 87.68; H, 6.75; N, 4.77.

When the above commented reactions were carried out at shorter reaction times, a mixture of the enamine with **5** or **6** was obtained respectively.

Characterization of 5. ^{1}H NMR (C_6D_6): δ 1.77 (s, 30H, C_5Me_5), 2.02 (s, 3H, *p-Me*C_6H_4), 5.96−7.77 (mc, 14H) (phenyl groups), 8.28 (s, 1H, ═CH).

Characterization of 6. ^{1}H NMR (C_6D_6): δ 1.75 (s, 30H, C_5Me_5), 2.08 (s, 3H, *p-Me*C_6H_4), 5.50−5.70 (mc, 14H) (phenyl groups), 5.85 (br, 1H, OH), 9.38 (s, 1H, ═CH). ^{13}C{^{1}H} NMR (C_6D_6): δ 12.1 (C_5*Me*$_5$), 20.4 (*p-Me*C_6H_4), 108.5 (Ph_2*C*), 114.3 (*C*H═N), 125.7 (*C*$_5Me_5$), 126.7, 126.9, 127.2, 127.5, 127.7, 128.3, 128.7, 129.5, 129.8, 130.2, 130.5, 130.8, 139.2, 139.9 (C phenyl groups), 129.2, 146.0, 148.2, 151.3 (C_{ipso} phenyl groups).

Reactions of 3 with H$_2$. The reaction of **3** with H_2 was monitored by NMR. Thus, when H_2 was bubbled into a C_6D_6 solution (0.7 mL) of **3** (30 mg, 0.05 mmol), a fast color change from red to deep green was observed which corresponds to the formation of **7**, which was spectroscopically characterized. However, when the H_2 was removed from the NMR tube solution of **7**, a change to the initial red color was observed, and both the disappearance of **7** and the formation of **3** were spectroscopically established. Attempts to isolate **7** to preparative scale were unsuccessful because, on removing the H_2 atmosphere from the green reaction solution of **7**, a red solution of the starting complex **3** was formed.

Characterization of 7. ^{1}H NMR (C_6D_6): δ 1.76 (s, 30H, C_5Me_5), 2.07 (s, 3H, *p-Me*C_6H_4), 4.97 (s, 1H, CH-N) 5.50 (br, 1H, Ti-H), 6.20−7.50 (mc, 14 H, phenyl groups). ^{13}C{^{1}H} NMR: δ 12.4 (C_5*Me*$_5$), 20.8 (*p-Me*C_6H_4), 122.1 (*C*$_5Me_5$), 126.9 (Ph_2*C*═C), 123.8, 123.9, 124.1, 124.3, 125.7, 125.9, 126.3, 127.0, 127.2, 127.6, 128.2, 128.4, 129.1, 130.5, 130.8 (C phenyl groups and *C*H-N), 128.1, 139.6, 140.7, 142.4 (C_{ipso} phenyl groups).

X-ray Data Collection, Structure Determination, and Refinement of 3. A suitable crystal was sealed in a Lindemann capillary under nitrogen and used for data collection. The crystallographic data are summarized in Table 2.

Accurate unit cell parameters were determined by least-squares refinement of the setting angles of 32 randomly distributed and carefully centered reflections with θ in the range 8−18°. The data collection was performed on a Philips

Table 2. Crystal Data and Structure Refinement for 3[a]

empirical formula	$C_{41}H_{47}NTi$
fw	601.70
temperature	293(2) K
wavelength	0.710 73 Å
cryst syst	monoclinic
space group	*C*2/*c*
unit cell dimensions	$a = 14.969(5)$ Å $b = 13.830(5)$ Å, $\beta = 101.78(2)$° $c = 16.703(5)$ Å
volume	3385(2) $Å^3$
Z	4
density (calcd)	1.181 Mg/m^3
abs coeff	0.281 mm^{-1}
F(000)	1288
cryst size	0.15 mm × 0.23 mm × 0.35 mm
θ range for data coll	3.20−27.02°
index ranges	$-19 \leq h \leq 18$, $-17 \leq k \leq 17$, $0 \leq l \leq 21$
no. of reflns collected	7204
no. of independent reflns	3694 [R(int) = 0.0755]
refinement method	full-matrix least-squares on F^2
data/restraints/params	3586/80/296
goodness-of-fit on F^2	0.952
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0791$, w$R_2 = 0.1998$
R indices (all data)	$R_1 = 0.1540$, w$R_2 = 0.2868$
largest diff peak and hole	0.590 and −0.620 e $Å^{-3}$
weighting scheme, *a*, *b*	0.1604, 0.0000

[a] GOF = $[\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$. $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$.

PW 1100 diffractometer in the $\theta/2\theta$ scan mode at 293 K with a variable scan speed of 3−9.6° min^{-1} and a scan width of 1.20 + 0.34 tan θ. One standard reflection was monitored every 100 measurements, and no significant decay was noticed over the time of data collection. The individual profiles have been analyzed according to the method of Lehmann and Larsen.[19] Intensities were corrected for Lorentz and polarization effects and reduced to F_o^2. The structure was solved by direct methods (SIR92[20]) and refined by full-matrix least-squares on F^2 using SHELXL-93,[21] first with isotropic thermal parameters and then with anisotropic thermal parameters for all the non-hydrogen atoms. All the hydrogen atoms were placed at their geometric default distance calculated positions and refined "riding" on their parent carbon atoms. Attempts to solve the structure in the *Cc* space group to avoid the great disorder were unsuccessful. All calculations were carried out on the ENCORE 91 of the Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma. The programs Parst[22] and ORTEP[23] were also used. The final atomic coordinates are provided in the Supporting Information.

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Supporting Information Available: Tables of final atomic coordinates for the non-hydrogen and the hydrogen atoms, anisotropic thermal parameters, complete list of bond distances and angles, and complete crystallographic data for **3** (7 pages). Ordering information is given on any current masthead page.

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