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Reactions of *in situ* generated (η^2-phenyltrimethylsilylacetylene)zirconocene

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Abstract

The five-membered metallacycle $Cp_2\overline{Zr(CR^1{=}CR^2CR^2{=}C}R^1)$ (**1**, $R^1 = SiMe_3$, $R^2 = Ph$) is a suitable starting material for the *in situ* generation of the reactive (η^2-phenyltrimethylsilylethyne)zirconocene (**3**). Thus, thermolysis of **1** (70 °C) with trimethylphosphane gives $Cp_2Zr(Me_3SiC{\equiv}CPh)(PMe_3)$ (**8**) and free $Me_3SiC{\equiv}CPh$ (**4**). Subsequent reaction of **8** with acetophenone produces $Cp_2\overline{Zr[CR^1{=}CR^2CMePhO}]$ (**9**, $R^1 = SiMe_3$, $R^2 = Ph$). Thermolysis of **1** in the presence of $CpW(CO)_3H$ also results in the liberation of one equivalent of **4**. The reactive intermediate **3** is protonated to give $Cp_2Zr(CR^1{=}CHR^2)(\mu\text{-}OC)W(CO)_2Cp$ (**12**, $R^1 = SiMe_3$, $R^2 = Ph$). Treatment of **1** with $[HNEt_3][BPh_4]$ in acetonitrile gives the cationic $Cp_2\overline{Zr(CR^1{=}CR^2CMe{=}N}H)(CH_3CN)^+$ (**13a**: $R^1 = SiMe_3$, $R^2 = Ph$) and its regioisomer **13b** (R^1 and R^2 exchanged). There is evidence that the complexes **13** are formed by acetonitrile addition to thermally-generated **3** to give $Cp_2\overline{Zr(CR^1{=}CR^2CMe{=}N})$, which is then subsequently protonated at the basic ring nitrogen. These reactions show that a readily available metallacyclopentadiene system can be used as a convenient synthetic equivalent of a very reactive (η^2-alkyne)metallocene complex by thermally induced equilibration in the presence of suitable trapping reagents.

Introduction

(η^2-Olefin)- and (η^2-acetylene)complexes of the group 4 bent metallocenes are very reactive organometallic building blocks with a formally d^2-configurated metal center and a 16-electron count [1]. The $Cp_2M(RCH{=}CHR)$ and $Cp_2M(RC{\equiv}CR)$ species sometimes serve as preparative sources of the elusive Cp_2M species themselves, i.e. they may undergo reactions involving loss of the alkene or alkyne ligand. More important, however, are various types of addition reactions, especially those of organic π-reagents that are taken up and CC-coupled with the η^2-organyl moiety to yield new metallacyclic bent metallocene complexes in which the central metal center is now formally d^0-configurated. Typical examples are the formation of metallacyclo-pentane and -pentene derivatives or even cyclic metaloxycarbene complexes by reaction of the (η^2-alkene and -alkyne)metallocene type reagents with olefins, alkynes, ketones, aldehydes, esters, or metal carbonyls [2,3]. In contrast,

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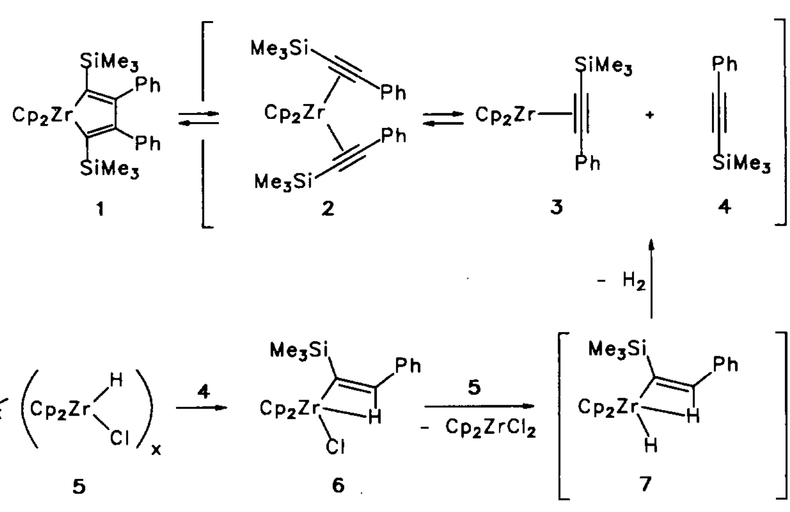
open-chain Cp_2M^{IV}-σ-hydrocarbyl products are formed by treatment with simple electrophiles [e.g. formation of $Cp_2M(X)CR{=}CHR$ by H–X addition to $Cp_2M(\eta^2$-$RC{\equiv}CR)$] [1].

In view of their rich chemistry it is unfortunate that stable, isolable examples of this class of compounds, such as e.g. $(Me_5C_5)_2Ti(\eta^2$-$CH_2{=}CH_2)$, are clearly the exception. More often the reactive $Cp_2M(RC{\equiv}CR)$ species have to be generated *in situ* from suitable precursors, such as the stable 18-electron $Cp_2M(L)(RC{\equiv}CR)$ complexes, in the presence of the respective trapping reagents. In some cases, dialkylmetallocenes unstable in respect of a β-hydrogen elimination/reductive elimination sequence have been very useful for *in situ* (η^2-alkene)MCp_2 generation [e.g. $Cp_2ZrCl_2 + 2^nBuLi \rightarrow [Cp_2ZrBu_2] \rightarrow Cp_2Zr(\eta^2$-1-butene) + butane] [1–3].

It is well known that two alkynes readily undergo coupling at the zirconocene unit to give the corresponding substituted 1,1-bis(cyclopentadienyl)zirconacyclopentadienes [4]. The rapid bis(η^2-alkyne)metallocene to metallacyclopentadiene conversion is sometimes a readily reversible reaction despite the fact that the equilibrium lies far over on the side of the metallacycle. Therefore reactive (η^2-alkyne)zirconocenes should in principle become available by shifting this equilibrium (e.g. **1** $\rightleftharpoons$ **2** $\rightleftharpoons$ **3** + alkyne **4**) by adding a suitable trapping reagent. We report here a series of experiments in which this synthetic approach was used.

Several examples involved use of the metallacycle 1,1-bis(cyclopentadienyl)-2,5-bis(trimethylsilyl)-3,4-diphenylzirconacyclopentadiene (**1**) as a starting material. Its bulky substituents seem to facilitate the ring-opening equilibration and elimination of one of the phenyltrimethylsilylacetylene building blocks in the presence of a scavenger. Furthermore complex **1** is easily available by hydrozirconation of the disubstituted acetylene. The formation of the five-membered metallacycle probably takes place via the β MHC-agostic alkenyl metallocene **6**. Its formation represents a typical example of an "anomalous" hydrozirconation reaction [5].

We report below some selected typical reaction sequences starting from **1** which probably proceed via *in situ* generated **3**, namely the addition of a ketone, a nitrile and some protonation reactions.

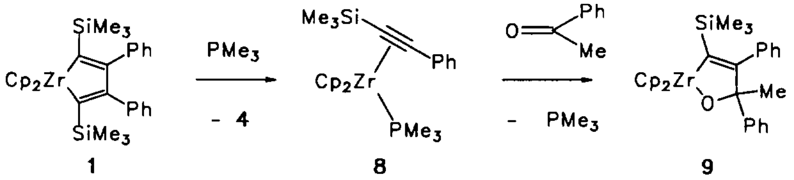


Scheme 1

Results and discussion

Reaction of (η^2-phenyltrimethylsilylacetylene)zirconocene with acetophenone

The reaction of **1** via **3** with acetophenone was not performed as a one pot reaction but carried out in a sequential manner via an isolated donor-ligand-stabilized intermediate. For this purpose we first treated the metallacycle 1,1-bis(η-cyclopentadienyl)-2,5-bis(trimethylsilyl)-3,4-diphenylzirconacyclopentadiene (**1**) with a tenfold excess of trimethylphosphane. Reaction took place smoothly at 70 ° C with liberation of one molar equivalent of phenyltrimethylsilylacetylene. The product (η^2-phenyltrimethylsilylacetylene)(trimethylphosphane)zirconium (**8**) was isolated as a yellow solid in 46% yield (IR: $\nu(C{\equiv}C) = 1620\ cm^{-1}$). Treatment of this with acetophenone (equimolar) in benzene at room temperature resulted in a rapid replacement of the phosphine, addition of the ketone and CC-coupling of the π-ligands at the zirconocene template to yield the oxametallacyclopentene **9** (ca. 50% yield of isolated product) [6].

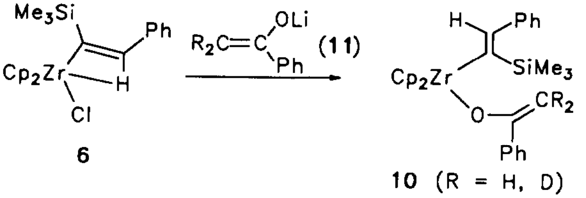


The alkenyl metallocene complex **6** contains a rather acidic β-agostic alkenyl hydrogen atom. We had previously shown that deprotonation at the alkenyl β-carbon atom can be achieved by a variety of hydrocarbyl groups σ-bonded to zirconium that can serve as intramolecular bases [5]. Having prepared the (η^2-$Me_3SiC{\equiv}CPh$) $ZrCp_2$/acetophenone addition product **9** as described above we were tempted to try to make the same complex by means of an intramolecular deprotonation using the metal-bonded enolate as a base.

The reaction of the agostic alkenyl metallocene complex **6** with the lithium enolate of acetophenone (ca. fourfold excess) [7] in ether was about complete in 30 h at ambient temperature. The σ-alkenyl zirconocene enolate complex **10** was isolated in ca. 70% yield. However, this product could not be converted into the metallacycle **9** by means of an intramolecular hydrogen transfer/ring closure reaction sequence as had been hoped. The probable reason for this unexpected behavior was that the alkenyl zirconium enolate complex did not contain an agostic β-alkenyl C–H metal interaction similar to that in the corresponding alkenyl zirconocene chloride starting material (**6**). This became apparent upon comparison of the relevant carbon NMR spectroscopic data for complexes **6** (agostic) and **10** (non-agostic). The agostic alkenyl zirconium complex is characterized by a =CH ^{13}C NMR absorption at δ 113.3 with a reduced $^1J(CH)$ coupling constant of 123 Hz [5,8], whereas **10** exhibits the analogous resonance at δ 143.8 ppm. The corresponding $^1J(CH)$ coupling constant is 147 Hz which is a normal value for an ordinary sp^2-C–H bond not involved in any significant metal–H–C interaction.

The resistance of the σ-alkenyl zirconocene enolate **10** towards further stabilizing reactions permitted a competition experiment aimed at gaining some information about the acidity of the agostic alkenyl β-CH bond in **6** relative to that in an ordinary organic carbonyl compound such as acetophenone. A solution of **6** and acetophenone in a toluene/tetrahydrofuran mixture (2.5 : 1) was treated with ethereal methyllithium. In this experiment, formation of the metallacycle **9** would indicate that deprotonation of the acidic agostic alkenyl hydrogen (intermolecularly by methyllithium or the preformed lithioacetophenone enolate or intramolecularly after methylation at zirconium) could compete with the α-deprotonation of the organic carbonyl compound. This product was not observed and we observed only the alkenyl zirconocene enolate **10**. This indicates that the kinetic acidity of the agostic alkenyl–CH–Zr moiety is substantially higher than that of the aromatic ketone (i.e. $pK_a > 19$).

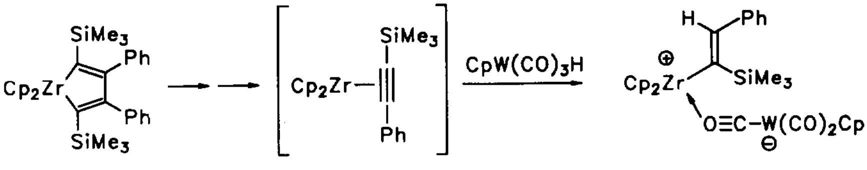
Of course, it had to be confirmed by a control experiment that the alkenyl zirconocene enolate was not simply the "thermodynamic sink" of the system looked at. This was demonstrated by treating a mixture of *E*-(2-phenyl-1-trimethylsilylethenyl)zirconocene chloride (**6**) and acetophenone-d_3 (**11**-d_3) with methyllithium. Formation of only the dideuterated complex $Cp_2Zr[C(SiMe_3){=}CHPh]OCPh{=}CD_2$ (**10**-d_2) clearly indicated that the alkenyl-β-CH bond had remained intact throughout the reaction.



Protonation and reaction with a nitrile

Zirconium to carbon σ-bonds can usually be readily cleaved by a protic reagent [9] and so it would require the $\mathbf{1} \rightleftharpoons \mathbf{2} \rightleftharpoons \mathbf{3} + \mathbf{4}$ equilibration to be quite fast to allow the (η^2-phenyltrimethylsilylacetylene)zirconocene intermediate **3** to compete successfully with the five-membered metallacycle **1** for a proton from a suitable source. The efficiency of establishing this equilibrium at least at elevated temperature could be demonstrated by using the organometallic Brönsted acid $CpW(CO)_3H$ for the $\mathbf{1} + H^+$ vs. $\mathbf{3} + H^+$ competition [10].

The reaction of the metallacycle **1** with $CpW(CO)_3H$ at 70 °C in toluene solution was virtually complete after 1 h. Phenyltrimethylsilylacetylene had been formed, and we isolated the alkenyl zirconocene-$OCW(CO)_2Cp$ adduct **12** as a yellow solid in about 36% yield. The Zr/W-bridging CO-unit shows spectroscopic features [$\nu(\mu\text{-CO}) = 1573\ cm^{-1}$] very similar to those for the analogously structured bimetallic complexes $Cp_2ZrCH_3(\mu\text{-OC})M(CO)_2Cp$ [$\nu(\mu\text{-CO}) = 1540$ (Cr), 1590 (Mo), 1540 (W) cm^{-1}] [10]. In complex **12** the alkenyl zirconocene moiety is non-agostic. As in **10**, the bonding of the oxygen-containing additional ligand probably lowers the Lewis-acidity of the early transition metal center beyond the critical threshold required for establishing the three-center two-electron metal–H–C bonding interaction. We therefore investigated whether trapping of **3** from the $\mathbf{1} \rightleftharpoons \mathbf{2} \rightleftharpoons \mathbf{3} + \mathbf{4}$ equilibration could be achieved by protonation in the presence of a non-nucleophilic anion (e.g. such as BPh_4^-).



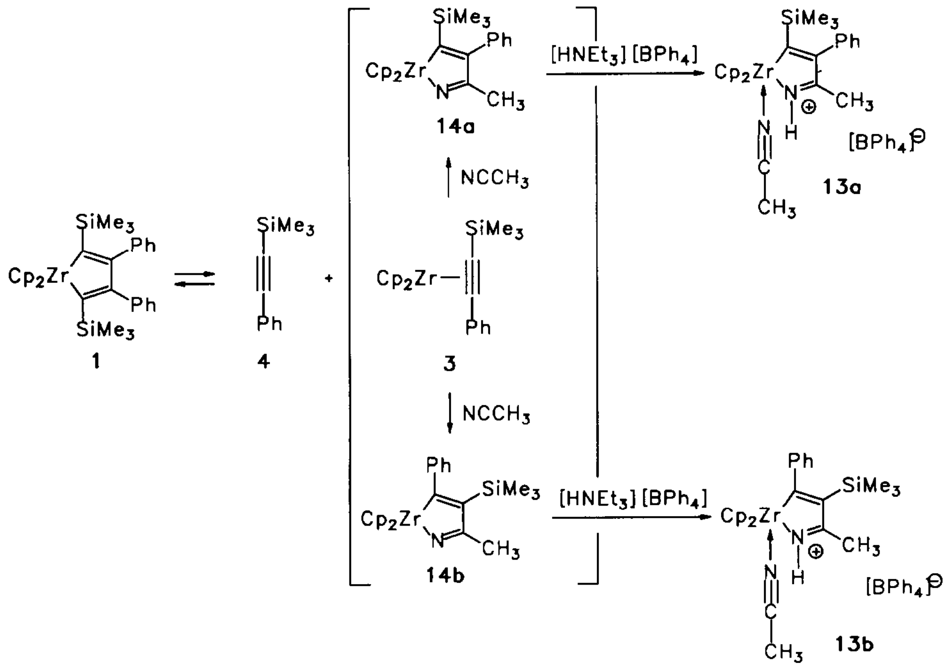
1 3 12

We treated the metallacyclopentadiene **1** with triethylammoniumtetraphenylborate ($[HNEt_3][BPh_4]$) at 70 °C in a toluene/acetonitrile solvent mixture using various $1/H^+$ ratios (from 1 : 1 to 1.6 : 1). The cationic metallacyclic products **13a** and **13b** were obtained in good yield with a variable regioisomeric ratio that approached the exclusive formation of complex **13a** with a decreasing $1/[HNEt_3][BPh_4]$ ratio [11].

Complex **13a** was characterized by IR resonances at $\nu = 3310$ cm^{-1} (N–H) and $\nu = 2305$, 2277 cm^{-1} (C≡N), probably split by Fermi resonance, a similar feature was previously observed for the cationic complexes $Cp_2TiMe(N{\equiv}CCH_3)^+$ (ν(CN) = 2310, 2282 cm^{-1}) and $Cp_2ZrMe(N{\equiv}CCH_3)^+$ (ν(CN) = 2303, 2273 cm^{-1}) [11,12]. The spectroscopic data for the regioisomeric zirconocenyl complex **13b** were obtained by using a **13a** : **13b** = 13 : 87 mixture that was formed by treating $[HNEt_3]^+$ with an excess of **1** (1 : 1.6) at 70 °C in acetonitrile/toluene. The data for complex **13b** are very similar to those for **13a** (e.g. ν(CN) = 2310, 2278 cm^{-1}; ν(N–H) = 3326 cm^{-1}). The relative assignment of the two regioisomers is based on a comparison of the UV–Vis spectra (recorded for pure **13a** and the 13 : 87 **13a**/**13b** mixture, respectively). Unfortunately, for both cations the UV–Vis-maxima were masked by the strong BPh_4-anion absorptions. However, complex **13b** shows a marked progressively increasing extinction at $\lambda < 490$ nm (which gives this complex its intense yellow color), whereas the isomer **13a** with the cross-conjugated π-chromophore has only a pale yellow color and shows no visible absorption at $\lambda > 450$ nm.

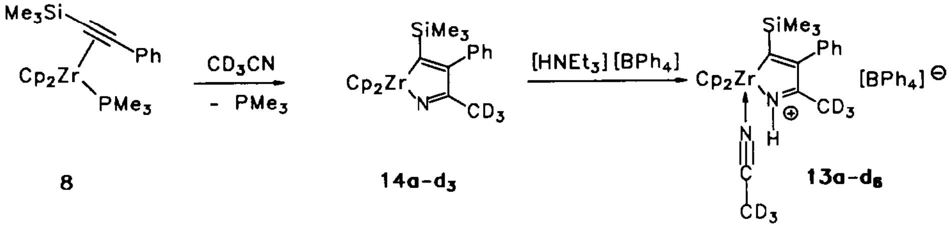
Complexes **13a** and **13b** could in principle have been formed by protonation of *in-situ*-generated (η^2-$Me_3SiC{\equiv}CPh$)$ZrCp_2$ (**3**), followed by nitrile insertion into the agostic β-alkenyl C–H bond. However, we think that these complexes are probably produced in a more conventional way, albeit also involving intervention of the *in-situ*-generated (η^2-alkyne)zirconocene complex **3**. We assume that the reactive alkyne-metallocene complex is efficiently trapped by the acetonitrile introduced into the system to solubilize the $[HNEt_3][BPh_4]$ proton source. Conventional [2 + 2 + 2] type cycloaddition at the metallocene template [4] then yields the regioisomeric neutral metallaheterocycles (**14a**/**14b**) [13], which are subsequently protonated by $[HNEt_3]^+$ to give the observed products. The factors important for influencing the balance between kinetic and thermodynamic control of this rather complicated reaction scheme, and thus determining the regiochemical outcome, are not yet completely understood, and more detailed experimental investigations will be needed.

Evidence in favour of the proposal that the cationic complexes **13** is formed via a conventional alkyne plus nitrile coupling at bis(cyclopentadienyl)zirconium came from an independent synthetic entry to the system. The isolated (η^2-alkyne) zirconocene complex (η^2-$Me_3SiC{\equiv}CPh$)(PMe_3)$ZrCp_2$ (**8**) was dissolved in acetonitrile ($N{\equiv}CCD_3$). During 10 min a yellow precipitate was formed, and this was probably the dimer of the azazirconacyclopentadiene system **14a**-d_3 [14]. The insoluble product slowly dissolved upon treatment with triethylammoniumtetraphenylborate



Scheme 2

to give the cationic zirconocene complex **13a**-d_6. In another experiment the reaction between (η^2-$Me_3SiC{\equiv}CPh$)(PMe_3)$ZrCp_2$ (**8**) and solvent CD_3CN was monitored directly by ^1H NMR spectroscopy. The reaction was complete within 10 min at ambient temperature. Free PMe_3 was observed in addition to a new product [δ −0.1 (s, 9H, $SiMe_3$), 5.8 (s, 10H, Cp)], which was probably the metallacycle **14a**-d_3. [$HNEt_3$][BPh_4] was then added to the clear solution and the rapid formation of the cationic nitrile adduct **13a**-d_6 observed by ^1H NMR spectroscopy.



Experimental section

Reactions with organometallic compounds were carried out under argon in Schlenk-type glassware. Solvents and reagents were dried and distilled under argon prior to use. The zirconocene complexes **1** and **6** were prepared as previously described [5]. The following spectrometers were used: Bruker WP 200 SY NMR spectrometer (^1H: 200 MHz, ^{13}C: 50 MHz); Nicolet 5 DXC FT-IR spectrometer; Perkin–Elmer 330 spectrophotometer (UV–Vis). Melting points (uncorrected) were determined in sealed capillaries with a SMP-20 (Büchi) apparatus. Elemental analyses were carried out at the Institut für Anorganische Chemie der Universität Würzburg.

[η^2-Phenyl(trimethylsilyl)ethyne](trimethylphosphane)zirconocene (**8**)

A solution of 1,1-Bis(cyclopentadienyl)-2,5-bis(trimethylsilyl)-3,4-diphenylzirconacyclopentadiene (**1**, 0.57 g, 1.16 mmol) and 1.80 mL (1.32 g, 17.4 mmol) of trimethylphosphane in 10 mL of toluene was heated for 1 h at 70 ° C. The solvent was then removed *in vacuo* at room temperature and the residue treated with 10 mL of pentane. The product (**1**) was filtered off and washed with two 3 mL portions of pentane to give 0.25 g (46%), m.p. 120 ° C (decomp.) Anal. Found: C, 60.36; H, 7.21. $C_{24}H_{33}PSiZr$ (471.6) calcd.: C, 61.08; H, 7.05%. IR (KBr): $\nu = 1620$ cm^{-1}. ^{1}H NMR (benzene-d_6): δ 0.28 (s, 9H, $SiMe_3$); 0.79 (d, 9H, ^2J(PH) 6 Hz, PMe_3); 5.32 (d, 10H, ^3J(PH) 1.8 Hz, Cp); 6.65–7.20 (m, 5H, Ph). ^{13}C NMR (benzene-d_6): δ 1.7 (^1J(CH) 118 Hz, $SiMe_3$); 17.4 (^1J(PC) 16 Hz, ^1J(CH) 131 Hz, PMe_3); 103.1 (Cp); 122.0, 123.1, 127.6, 157.9 (Ph); 177.4 (^2J(PC) 8Hz); 181.0 (^2J(PC) 19Hz, C≡C). ^{31}P NMR (benzene-d_6): δ 2.2.

Reaction of [η^2-phenyl(trimethylsilyl)ethyne](trimethylphosphane)zirconocene (**8**) *with acetophenone*

A solution of 90 mg (0.19 mmol) of **8** and 22 μL (0.20 mmol) of acetophenone in benzene-d_6 was stirred for 1 h at ambient temperature. ^{1}H NMR spectroscopy revealed that the reaction was practically complete after this time, and that only one organometallic product was present. The solvent was removed *in vacuo* and the residue stirred with 3 mL of pentane. The yellow solid (**9**) was filtered off and washed three times with 2 mL portions of pentane. Yield: 50 mg (51%), m.p. 167–169 ° C Anal. Found: C, 66.08; H, 6.32. $C_{29}H_{32}OSiZr$ (515.6) calcd.: C, 67.50; H, 6.26%. ^{1}H NMR (benzene-d_6): δ −0.13 (s, 9H, $SiMe_3$); 1.75 (d, 3H, CH_3); 6.17 (s, 5H, Cp); 6.20 (s, 5H, Cp); 6.75–7.45 (m, 10H, Ph). ^{13}C NMR (benzene-d_6): δ 3.8 (^1J(CH) 119 Hz, $SiMe_3$); 27.3 (CH_3); 95.0 (OC); 112.3 (Cp); 112.5, 126.1, 126.4, 126.8, 127.1, 127.4, 130.7, 145.4, 147.5, 176.3, 192.1 (arom. C and C=C).

Reaction of E-*(2-phenyl-1-trimethylsilylethenyl)zirconocene chloride* (**6**) *with the lithium enolate of acetophenone*

A solution of 230 mg (0.53 mmol) of **6** and 250 mg (1.98 mmol) of H_2C=CPhOLi in a mixture of ether (20 mL) and toluene (15 mL) was stirred for 30 h at room temperature. The solvent was evaporated *in vacuo* and the residue extracted with 20 mL of pentane and filtered. The solvent was removed from the clear filtrate to leave **10** as a yellow oil. Anal. Found: C, 66.11; H, 6.31. $C_{29}H_{32}OSiZr$ (515.6) calcd.: C, 67.50; H, 6.26%. IR (NaCl): ν 1686 cm^{-1}. ^{1}H NMR (benzene-d_6): δ 0.16 (s, 9H, $SiMe_3$); 4.06 and 4.67 (each s, 1H, =CH_2); 6.01 (s, 10H, Cp); 6.95–7.60 (m, 10H, Ph); 8.32 (s, 1H, =CHPh). ^{13}C NMR (benzene-d_6): δ 3.6 (^1J(CH) 119 Hz, $SiMe_3$); 87.1 (^1J(CH) 157 Hz); 111.8 (Cp); 125.8, 126.7, 128.0, 128.3, 128.4, 139.5, 142.8 (Ph; 1C not located); 143.8 (^1J(CH) 147 Hz); 166.0 (OC); 200.3 (ZrC).

Reaction of a mixture of **6** *and acetophenone with methyllithium*

To a sample of 1.10 g (2.51 mmol) of **6** and 0.39 g (3.25 mmol) of acetophenone in a toluene/tetrahydrofuran mixture (25 and 10 mL) at room temperature were added 7 mL of a 0.36 *M* ethereal methyllithium solution. The mixture was stirred for 24 h at 35 ° C. The solvent was removed *in vacuo* and the residue extracted with pentane (20 mL). Filtration of the extract and removal of the pentane left 0.97 g (74%) of **10** as a yellow oil.

*Reaction of **6** with acetophenone-*d_3 *and methyllithium*

To a solution of 0.33 g (0.76 mmol) of **6** and 0.74 g (7.63 mmol) of acetophenone-d_3 in 5 mL of toluene were added 2 mL of a 0.36 *M* ethereal methyllithium solution. ^{1}H NMR spectroscopy of a sample after 5 h at 35 ° C showed only the product **10**-d_2 in addition to some residual starting material. ^{1}H NMR of **10**-d_2 (benzene-d_6): δ 0.16 (s, 9H, $SiMe_3$); 6.01 (s, 10H, Cp); 6.95–7.60 (m, 10H, Ph); 8.32 (s, 1H, CH).

*(μ-Carbonyl-OC)[*E*-(2-phenyl-1-trimethylsilylethenyl)zirconocene](cyclopentadienyl)(tricarbonyl)tungsten (**12**)*

A mixture of 570 mg (1.00 mmol) of **1** and 334 mg (1.00 mmol) of (cyclopentadienyl)(hydrido)(tricarbonyl)tungsten in 10 mL of toluene was stirred for 1 h at 70 ° C with exclusion of light. The yellow solution turned orange during this time. It was concentrated to a volume of ca. 5 mL and then kept for 24 h at −25 ° C. The resulting yellow solid was filtered off and washed with pentane (5 × 2 mL) to give 260 mg (26%) of **12**, m.p. 118–119 ° C (decomp.) Anal. Found: C, 48.10; H, 4.43. $C_{29}H_{30}O_3SiWZr$ (729.4) calcd.: C, 47.71; H, 4.15%. IR (KBr): $\nu = 1927$, 1829 (C≡O), 1573 cm^{-1} (μ-CO). ^{1}H NMR (benzene-d_6): δ 0.08 (s, 9H, $SiMe_3$); 5.17 (s, 5H, WCp); 5.87 (s, 10H, $ZrCp_2$), 7.05–7.20 and 7.32–7.40 (m, 5H, Ph); 7.29 (s, 1H, CH); ^{13}C NMR (methylene chloride-d_2): δ 1.5 ($SiMe_3$); 88.0 (^1J(CH) 176 Hz, WCp); 112.8 (^1J(CH) 175 Hz, $ZrCp_2$); 128.1 (^1J(CH) 155 Hz); 128.4 (^1J(CH) 159 Hz); 128.7 (^1J(CH) 163 Hz); 129.4 (^1J(CH) 159 Hz, Ph, and =CH); 136.3 (Ph, *ipso*); 212.0, 223.1, 243.3.

Reaction of 1 with triethylammoniumtetraphenylborate

(a) *Equimolar:* A mixture of 340 mg (0.60 mmol) of **1** and 251 mg (0.60 mmol) of $[HNEt_3][BPh_4]$ in 10 mL of toluene/acetonitrile (1 : 1) was stirred for 1.5 h at 70 ° C. The solvent was removed *in vacuo* and the residue stirred with 20 mL of toluene. The resulting light-yellow precipitate was filtered off and washed with toluene (2 × 10 mL) and then pentane (10 mL) to yield 340 mg (71%) of **13a**, m.p. 173–175 ° C (decomp.). Anal. Found: C, 71.92; H, 6.19; N, 3.18. $C_{49}H_{51}BN_2SiZr$ (797.6) calcd.: C, 73.73; H, 6.45; N, 3.51. IR (KBr): $\nu = 3310$ (N-H), 3205, 2277 cm^{-1} (CN). UV (CH_3CN): $\lambda < 450$ nm. ^{1}H NMR (acetonitrile-d_3): δ −0.35 (s, 9H, $SiMe_3$); 1.77 (d, ^4J 1.3 Hz, 3H, CH_3); 1.95 (s, 3H, $NCCH_3$); 6.18 (s, 10H, Cp); 6.70–7.40 (m, 25H, Ph); 8.40 (broad s, 1H, NH). ^{13}C NMR (acetonitrile-d_3): δ 1.8 and 4.2 ($\mathit{C}H_3CN$ and $Si(\mathit{C}H_3)_3$); 26.8 (CH_3); 112.0 (Cp); 122.8, 126.6, 128.1, 128.8, 131.3, 136.7, 144.4, 154.6, 164.8, 193.0, 237.8.

(b) *With an excess of 1:* A mixture of 550 mg (0.96 mmol) of **1** and 250 mg (0.59 mmol) of $[HNEt_3][BPh_4]$ in 10 mL of toluene/acetonitrile (1 : 1) was stirred for 1.5 h at 70 ° C. The solution was concentrated to ca. 2 mL to give some precipitate. Toluene (20 mL) was added and the precipitate was filtered off, then washed with toluene (2 × 5 mL) and pentane (5 mL) to yield 370 mg (79%) of a yellow powder of a 87 : 13 mixture of **13b** and **13a**, m.p. 188–189 ° C (decomp.). Anal. of the mixture. Found: C, 73.98; H, 6.40; N, 3.19. $C_{49}H_{51}BN_2SiZr$ (797.6) calcd.: C, 73.73; H, 6.45;

N, 3.51. UV (CH_3CN): $\lambda < 490$ nm. **13b**: IR (KBr): $\nu = 3326$ (N–H), 2310, 2278 cm^{-1} (CN). ^1H NMR (acetonitrile-d_3): δ −0.12 (s, 9H, $SiMe_3$); 1.95 (s, 3H, CH_3CN); 2.39 (d, ^3J 1.3 Hz, 3H, CH_3); 5.98 (s, 10H, Cp); 6.70–7.40 (m, 25H, Ph); 8.15 (broad s, 1H, N–H). ^{13}C NMR (acetonitrile-d_3): δ 2.9 and 4.8 (CH_3CN and $Si(CH_3)_3$); 28.6 (^1J(CH) 130 Hz, CH_3); 112.4 (Cp); 123.4, 125.5, 126.9, 127.2, 129.4, 137.4, 148.6, 154.0, 165.4, 197.0, 254.3.

*Reaction of (η^2-phenyltrimethylsilylethyne)(trimethylphosphane)zirconocene (**8**) with acetonitrile-d_3 and subsequently with triethylammoniumtetraphenylborate*

(a) A solution of 30 mg (0.06 mmol) of **8** in 0.5 mL of acetonitrile-d_3 was stirred at room temperature for 10 min, during which a yellow solid separated. The supernatant liquid was decanted and the yellow precipitate dried *in vacuo* then treated with 30 mg (0.07 mmol) of triethylammoniumtetraphenylborate, 0.5 mL of benzene-d_6, and 0.5 mL of acetonitrile-d_3. After 3 d the solid had almost completely dissolved. Complex **13a**-d_6 was the only organometallic product detected by ^1H NMR spectroscopy.

(b) A sample of 30 mg (0.06 mmol) of **8** was dissolved in a mixture of 0.2 mL of acetonitrile-d_3 and 0.2 mL of benzene-d_6. The reaction was monitored directly by ^1H NMR spectroscopy. Almost complete transformation of the starting material had occurred after 8 min. In addition to PMe_3 only one new product, probably **14a**-d_3, was present [^1H NMR: δ −0.09 (s, 9H, $SiMe_3$); 5.77 (s, 10H, Cp)]. Then 30 mg (0.07 mmol) of $[HNEt_3][BPh_4]$ were added. Formation of **13a**-d_6 was monitored by ^1H NMR: δ −0.16 (s, 9H, $SiMe_3$); 5.93 (s, 10H, Cp); 6.60–7.40 (m, 25H, Ph); 8.15 (broad s, 1H, NH).

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