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Reactions of β-CH Agostic Alkenylzirconocene Complexes

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Hydrozirconation of phenyl(trimethylsilyl)acetylene at ambient temperature yields mixtures of the β-CH agostic alkenylmetallocene complex $Cp_2Zr(Cl)C(SiMe_3){=}CPhH$ (**2a**), zirconocene dichloride (**5**), and the metallacyclopentadiene $Cp_2ZrC(SiMe_3){=}CPhCPh{=}C(SiMe_3)$ (**3a**). The last product probably is formed from **2a** and $[Cp_2Zr(H)Cl]$ via hydride/chloride exchange, producing the intermediate $Cp_2Zr(H)C(SiMe_3){=}CPhH$ (**4a**), which loses dihydrogen and adds 1 equiv of $Me_3SiC{\equiv}CPh$ to give **3a**. Photolysis of **2a** also yields a mixture of **3a** and **5**. Complex **3a** was characterized by X-ray diffraction. It crystallizes in space group $C2/c$ with cell parameters $a = 21.241$ (4) Å, $b = 10.881$ (2) Å, $c = 14.692$ (3) Å, $\beta = 116.91$ (1)°, $Z = 4$, $R = 0.035$, and $R_w = 0.039$. The reaction of **2a** with lithioacetylides $LiC{\equiv}CR$ ($R = CH_3$, Ph) produces metallacycles as well. The complexes $Cp_2ZrC(SiMe_3){=}CPhCH{=}CR$ (**3b,c**) are thought to be produced via β-CH agostic alkenylalkynylmetallocene intermediates $Cp_2Zr(C{\equiv}CR)C(SiMe_3){=}CPhH$ (**4b,c**). Intramolecular abstraction of the acidic agostic alkenyl proton by the σ-alkynyl ligand directly leads to the formation of bis(alkyne)metallocene complexes (**7b,c**), which undergo rapid ring closure to give **3b** and **3c**, respectively. Complex **3c** (R = Ph) was characterized by X-ray diffraction. It crystallizes in space group $P2_1/n$ with cell parameters $a = 7.798$ (1) Å, $b = 20.695$ (2) Å, $c = 15.549$ (2) Å, $\beta = 100.15$ (1)°, $Z = 4$, $R = 0.035$, and $R_w = 0.047$. From EHMO model calculations it is suggested that the "anomalous" hydrozirconation of diphenylacetylene, for example, which cleanly gives Cp_2ZrCl_2 and the metallacycle $Cp_2ZrCPh{=}CPhCPh{=}CPh$, also proceeds via intermediate β-CH agostic (alkenyl)$Cp_2Zr(X)$ type intermediates.

Introduction

Examples of metal complexes showing three-center-two-electron interactions between a transition-metal center and an adjacent C-H bond are abundant. Many of these M-H-C "agostic" compounds have been structurally and spectroscopically well characterized.[1] With regard to their chemical reactivity it still seems to be an open question whether the formation of the agostic metal-H-C interaction leads to an activation of the otherwise unactivated C-H bond for chemical functionalization. Experimental studies aimed at answering this important question are still very scarce,[2] being vastly outnumbered by the many structurally oriented investigations of agostic metal complexes.

We have recently found that alkenylzirconocene complexes $Cp_2Zr(Cl)CR{=}CR'H$ show an agostic interaction between the 16-electron early-transition-metal center and the alkenyl β-C-H bond, provided sufficiently bulky substituents R and R′ force the $=CR'H$ hydrogen into the vicinity of the zirconium.[3,4] The system where R is $-SiMe_3$ and R′ is Ph has been subjected to reactions with CO and an isonitrile.[5] The zirconium to carbon σ-bond turned out to be more reactive toward these reagents than the M-H-C moiety. However, there is evidence that the β-CH-M agostic complex $Cp_2Zr(Cl)C(SiMe_3){=}CPhH$ does undergo reactions involving the three-center-two-electron linkage, proceeding with cleavage of the alkenyl (sp^2) C-H σ-bond. We here report several examples where rupture of the "agostically activated" carbon to hydrogen bond is a prominent feature of the specific reaction course taken.

Results and Discussion

Starting from the agostic complex $Cp_2Zr(Cl)C(SiMe_3){=}CPhH$ (**2a**), we have carried out several reactions that actively involve the alkenyl β-CH bond. The conclusions drawn from our experimental studies have been aided by the results from model calculations with the EHMO method. A brief description of these theoretical studies follows after a discussion of the experimental investigation.

Experimental Studies. Hydrozirconation of phenyl(trimethylsilyl)acetylene at room temperature yields three reaction products. The formation of the alkenylzirconocene chloride **2a** is quite expected. X-ray crystallography revealed for this product that the bulky trimethylsilyl substituent is located at the α-position at the alkenyl ligand. Moreover, the presence of a pronounced agostic alkenyl β-C-H-Zr interaction was evident from the X-ray crystal structure analysis as well as very characteristic NMR data ($=CH-$: $\delta = 8.59$ (^1H); $\delta = 113.3$, $^1J_{CH} = 123$ Hz (^{13}C)).[4]

In addition to the main product **2a**, the two other products Cp_2ZrCl_2 (**5**) and the metallacycle **3a** are always formed when $Me_3SiC{\equiv}CPh$ is exposed to the hydrozirconation reagent $[Cp_2Zr(H)Cl]_x$ (**1**) at ambient tem-

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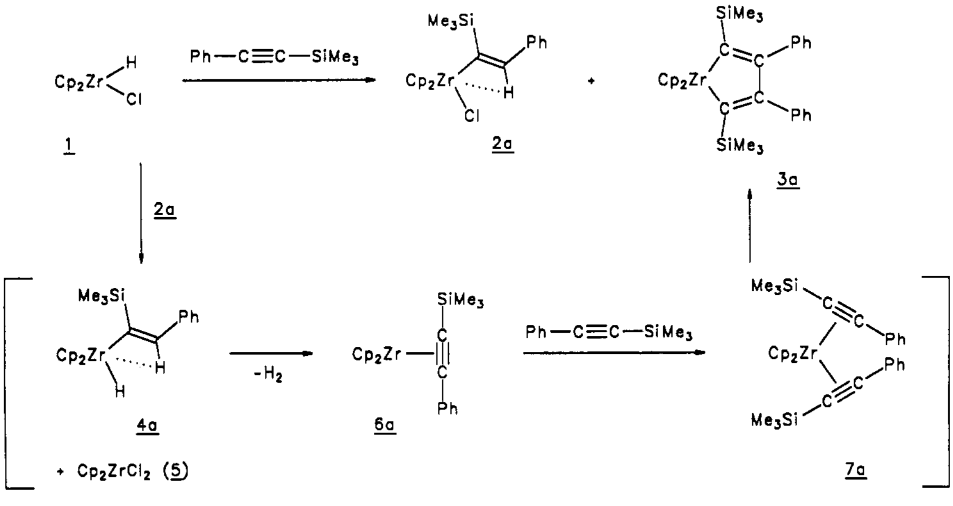
Scheme I



perature. Products **5** and **3a** are obtained in equimolar ratios. The **2a**:**5** + **3a** ratio varies somewhat with the reaction conditions. Typically, about one-third of the reaction mixture consists of the normal hydrozirconation product **2a**.

The products **5** and **3a** of the anomalous course of the hydrozirconation reaction are probably secondary reaction products derived from the β-CH agostic alkenylzirconocene complex **2a** (see Scheme I). It is likely that **2a** reacts in the mixture with additional zirconium hydride reagent by means of chloride vs hydride exchange.[6] This metathesis reaction furnishes the observed Cp_2ZrCl_2 product (**5**) plus a reactive alkenylzirconocene hydride intermediate (**4a**). Ordinary alkenylzirconocene hydrides typically decompose by thermally induced reductive-elimination pathways to give the corresponding alkenes. The β-CH agostic complex **4a** reacts quite differently, namely by loss of dihydrogen[7] to give a coordinatively unsaturated alkyne–zirconocene species (**6a**). Addition of $Me_3SiC{\equiv}CPh$ gives **7a**, which undergoes rapid subsequent ring closure[8] to yield the observed metallacycle **3a**. The key step in this proposed reaction sequence is the reaction of the zirconium-bound hydride ligand acting as a base in **4a** with the agostic β-alkenyl hydrogen, which is probably being somewhat acidified by its interaction with the adjacent Lewis-acidic early-transition-metal center.[9]

It would have been desirable to have Zr–alkyl derivatives of **4a** available to test if they decomposed analogously by intramolecular alkenyl β-hydrogen abstraction to form **6a** and an alkane. However, attempts to prepare $Cp_2Zr(CH_2Ph)C(SiMe_3){=}CPhH$, for example, by the reaction of **2a** with benzylmagnesium halides have failed so far. Surprisingly, the reaction of **2a** with $PhCH_2MgBr$ took an unexpected different course, cleanly producing $Cp_2Zr(Br)C(SiMe_3){=}CPhH$ (**2b**), i.e. proceeding preferrentially via halide/halide exchange rather than via benzyl anion substitution. Complex **2b** was unambiguously identified by an X-ray crystal structure analysis.[4b] The detailed course of its formation remains to be established.

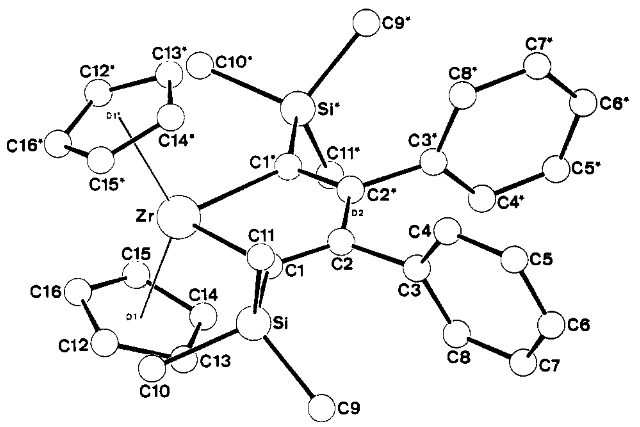
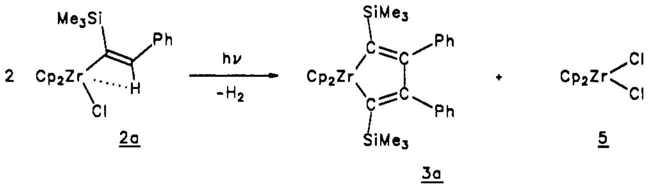


Figure 1. View of the molecular structure of **3a**.

On a preparative scale the metallacyclic product **3a** can best be synthesized by photolysis of the alkenylzirconocene chloride **2a**. UV irradiation of **2a** in toluene (HPK 125, Pyrex filter) rapidly yields a 1:1 mixture of zirconocene dichloride (**5**) and **3a**. Photochemically induced σ-ligand-exchange reactions of alkenylzirconocene halides to give mixtures of Cp_2ZrCl_2 and dialkenylzirconocene complexes are well-known.[10] There is evidence that such reactions proceed by means of a radical mechanism via the Cp_2ZrX chain carrying organometallic radicals. Usually, the resulting dialkenylzirconocene products are not stable under the reaction conditions but rearrange by σ-ligand coupling to give (*s-trans*-η^4-conjugated diene)zirconocene complexes.[11] The presumably formed primary product in the photolysis of **2a**, $Cp_2Zr[-C(SiMe_3){=}CPhH]_2$, apparently favors a different route of stabilization by a subsequent chemical reaction. Instead of the two very bulky σ-alkenyl ligands being coupled to form a tetrasubstituted conjugated diene ligand, dihydrogen is lost. The resulting $Cp_2Zr(Me_3SiC{\equiv}CPh)_2$ then undergoes the



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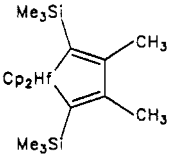
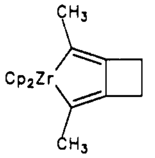
usual rapid bis(alkyne)metallocene to metallacyclopentadiene ring-closure reaction[8] to give the observed product **3a**.

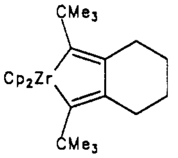
Complex **3a** was characterized by an X-ray crystal structure analysis. Most importantly, this has established the regiochemistry of the alkyne–alkyne CC coupling at the zirconium center during the **7a** to **3a** rearrangement. The molecular structure of **3a** (see Figure 1) shows that both bulky trimethylsilyl groups end up at the 2- and 5-positions of the metallacycle; i.e., they are bonded to the carbon centers C(1) and C(1)* adjacent to the transition-metal center. The phenyl groups prefer to be bonded to the β-carbon atoms in the ring. This arrangement of substituents is not without precedence. Eisch et al. observed the same regioselectivity upon $Me_3SiC{\equiv}CR$ insertion into a Ti–CH_3 bond to give the cationic titanocene complex $[Cp_2TiC(SiMe_3){=}CRCH_3]^+$.[12] Coupling of $Me_3SiC{\equiv}CCH_3$ at bis(cyclopentadienyl)hafnium produced **3e**, also exhibiting the large Me_3Si groups at the α-positions.[13] Similarly, placing the Me_3C substituents adjacent to the metal was no hindrance for making **3g** by acetylene coupling.[14] Therefore, we note that the observed regiochemistry of the **7a** → **3a** coupling reaction is quite as expected.[15] Steric features seem to dominate in the ring-closure reaction. It appears to be favorable if the bulky substituents are occupying the sterically free lateral sectors in the central plane of the bent metallocene unit.[16]



3e



3f



3g

In **3a** the C(1)–Si vectors are arranged almost perfectly collinear. As a result the Zr–C(1)–Si (129.7 (1)°) and Zr–C(1)–C(2) angles (105.9 (2)°) deviate from typical C(sp^2) bonding angles. The angles around C(2) are normal (C(1)–C(2)–C(2)* = 122.8 (2)°; C(1)–C(2)–C(3) = 121.4 (2)°). The Zr–C(1) bond in **3a** (2.265 (2) Å) is longer than in **3f** (2.204 (2) and 2.211 (2) Å) or **3g**[14] (2.210 (2) and 2.217 (2) Å). However, this bond length is quite similar to the Zr–C^α distances (2.265 (6) and 2.250 (5) Å) observed for $\mathrm{Cp_2\overline{ZrCPh{=}CPhCPh{=}CPh}}$ **3d**.[17]

The standard bond length for a tetrasubstituted C=C double bond in organic molecules is 1.331 Å; for a single bond between two conjugated sp^2-hybridized carbon centers it is 1.455 Å.[18] With 1.511 (3) Å, the C(2)–C(2)* bond in **3a** is somewhat longer than the statistical standard, as is the C(1)–C(2) bond at 1.363 (3) Å. However, this seems to be typical for the known examples of such metallacycles (**3d**, $C^\alpha{=}C^\beta$ (two independent values) 1.363 (7) and 1.358 (8) Å, C^β–$C^{\beta*}$ 1.500 (7) Å; **3e**, 1.370 (8) and 1.346 (9) Å, 1.503 (9) Å; **3f**, 1.330 (3) and 1.324 (3) Å, 1.565 (3) Å; **3g**, 1.360 (3) and 1.335 (3) Å 1.547 (3) Å). The rings of the phenyl substituents of **3a** at C(2)/C(2)* are bisecting the Zr,C(1),C(2),C(2)*,C(1)* ring plane (85°). The C(2)–C(3) bond length is 1.510 (3) Å, deviating slightly from the statistically expected standard value of 1.488 Å for a C(sp^2)–C(ar) single bond in an unconjugated situation.[18] The conformational arrangement of the substituents and the observed bonding parameters seem to be the consequence of trying to avoid too much unfavorable interaction between the six bulky groups attached to the rather small central metallacyclic framework of **3a**

Table I. Selected Bond Distances (Å) and Bond Angles (deg) of 3a

Zr–D(1)	2.230 (3)	Si–C(1)	1.879 (3)
Zr–D(2)	2.847 (3)	Si–C(9)	1.865 (4)
Zr–C(1)	2.265 (2)	Si–C(10)	1.879 (3)
Zr–C(12)	2.510 (3)	Si–C(11)	1.850 (4)
Zr–C(13)	2.511 (3)	C(1)–C(2)	1.363 (3)
Zr–C(14)	2.513 (3)	C(2)–C(3)	1.510 (3)
Zr–C(15)	2.528 (4)	C(2)–C(2*)	1.511 (3)
Zr–C(16)	2.531 (4)		
C(1*)–Zr–C(1)	82.6(1)	C(10)–Si–C(1)	111.0 (1)
D(1*)–Zr–D(1)	136.3 (1)	C(9)–Si–C(1)	117.0 (1)
D(2)–Zr–D(1)	111.9 (1)	C(2)–C(1)–Si	124.4 (2)
D(1)–Zr–C(1)	106.7 (1)	C(2)–C(1)–Zr	105.9 (2)
C(11)–Si–C(10)	106.9 (2)	Si–C(1)–Zr	129.7 (1)
C(11)–Si–C(9)	107.5 (2)	C(2*)–C(2)–C(3)	115.8 (2)
C(11)–Si–C(1)	109.8 (1)	C(2*)–C(2)–C(1)	122.8 (2)
C(10)–Si–C(9)	104.0 (2)	C(3)–C(2)–C(1)	121.4 (2)

Table II. Atomic Fractional Coordinates and Equivalent Isotropic Thermal Parameters (Å²), with Standard Deviations in Parentheses, of 3a[a]

atom	x	y	z	U_{eq}
Zr	0.0000	0.2619 (1)	0.2500	0.047
Si	0.1681 (1)	0.1102 (1)	0.2848 (1)	0.058
C(1)	0.0752 (1)	0.1055 (2)	0.2687 (2)	0.045
C(2)	0.0384 (1)	0.0003 (2)	0.2611 (2)	0.043
C(3)	0.0732 (1)	−0.1243 (2)	0.2780 (2)	0.046
C(4)	0.0803 (1)	−0.1862 (3)	0.2013 (2)	0.063
C(5)	0.1166 (2)	−0.2960 (3)	0.2202 (3)	0.086
C(6)	0.1459 (2)	−0.3464 (3)	0.3150 (4)	0.091
C(7)	0.1385 (2)	−0.2888 (3)	0.3919 (3)	0.087
C(8)	0.1018 (2)	−0.1783 (3)	0.3734 (2)	0.065
C(9)	0.2330 (2)	0.0034 (3)	0.3805 (3)	0.086
C(10)	0.2083 (2)	0.2664 (3)	0.3276 (3)	0.090
C(11)	0.1681 (2)	0.0793 (4)	0.1609 (3)	0.098
C(12)	0.0810 (2)	0.3833 (3)	0.4039 (2)	0.077
C(13)	0.0781 (2)	0.2657 (3)	0.4392 (2)	0.078
C(14)	0.0100 (2)	0.2491 (4)	0.4268 (2)	0.091
C(15)	−0.0276 (2)	0.3568 (5)	0.3848 (3)	0.098
C(16)	0.0164 (2)	0.4361 (3)	0.3729 (3)	0.091

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\bar{a}_i\cdot\bar{a}_j$.

Complex **2a** reacts cleanly with lithioacetylenides LiC≡CR (R = CH_3, Ph) to give a single reaction product each. Their spectroscopic features (e.g. ^{13}C NMR, doublet at δ 122.4 ($^1J_{CH}$ = 148 Hz) or δ = 121.5 ($^1J_{CH}$ = 149 Hz), respectively) in addition to an X-ray crystal structure analysis (see below) assign to them the five-membered metallacyclic structures **3b** and **3c**, respectively.

Probably, the LiC≡CR reagent initially substituted the chloride ligand of **2a** to yield the alkenylalkynylmetallocene system (**4b,c**). These complexes are not stable under the reaction conditions, however.[19] Their β-CH agostic

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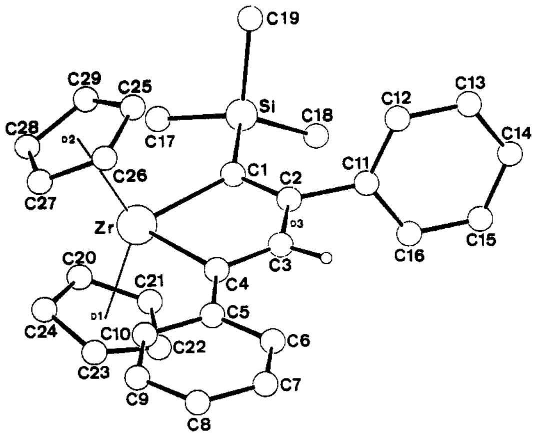
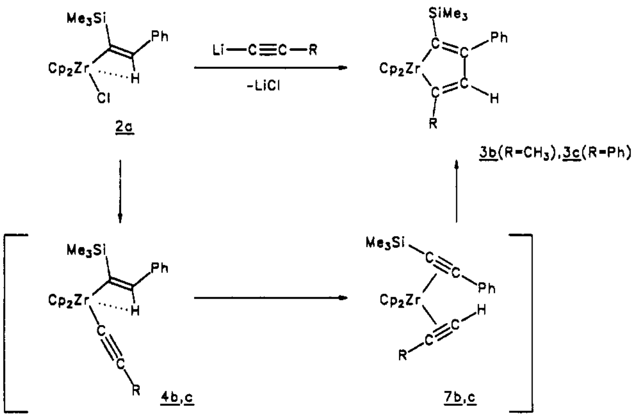


Figure 2. Projection of the molecular structure of **3c**, as revealed by X-ray diffraction.

Scheme II



structural feature allows an easily proceeding intramolecular deprotonation by the σ-alkynyl ligand to give the bis(alkyne)zirconocene precursor (**7b,c**) of the eventually obtained metallacycle (**3b,c**). Again, the ring-closure reaction shows the regiochemical characteristics expected from selected model studies, due to which the substitution pattern for the finally obtained zirconacyclopentadiene is reminiscent of the specific orientation of both π-alkyne ligands on the Cp_2Zr unit in its direct bis(alkyne)$ZrCp_2$ complex precursor.[8b]

The X-ray crystal structure analysis reveals the usual planar metallacyclic framework of the zirconacylopentadiene **3c**. Bond distances within the metallacycle are 2.244 (2) and 2.246 (2) Å for Zr–C(1) and Zr–C(4), respectively. The carbon–carbon distances are 1.371 (3), 1.482 (3), and 1.359 (3) Å for C(1)–C(2), C(2)–C(3), and C(3)–C(4), respectively. The bonds to the substituents at the α-carbon atoms are slightly bent away from zirconium (angles Zr–C(1)–Si = 132.3 (1)°, Zr–C(1)–C(2) = 102.2 (2)°, Zr–C(4)–C(5) = 135.5 (2)°, Zr–C(4)–C(3) = 102.2 (2)°). The phenyl group at C(2) is rotated away from the plane of the metallacycle by 78°, whereas the phenyl substituent at C(4) is lying in the metallocene central plane (θ = 5°), thus allowing for full electronic conjugation with the metallacyclic π-system. Not unexpectedly, the C(2)–C(11) distance (1.502 (3) Å) is somewhat longer than the C(4)–C(5) bond (1.477 (3) Å).

Model Calculations. The most interesting result from the X-ray investigations carried out on **2a** is the relatively small Zr–C(1)–C(2) angle of 89.9°. In a preceding paper[4b] we rationalized the deviation of this angle from 120° by a cooperation of steric and electronic effects, both leading to an agostic[1] interaction of the C(2)–H bond. To study a possible agostic interaction in the proposed intermediates **2d** and **4a**, we minimized the total energy of both compounds as a function of α and β (see structure a) by using

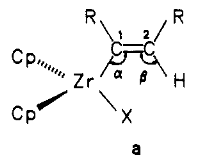
Table III. Selected Bond Distances (Å) and Bond Angles (deg) of 3c

Zr–D(1)	2.218 (3)	Zr–C(27)	2.504 (3)
Zr–D(2)	2.225 (3)	Zr–C(28)	2.518 (3)
Zr–D(3)	2.766 (3)	Zr–C(29)	2.544 (3)
Zr–C(1)	2.244 (2)	Si–C(1)	1.851 (2)
Zr–C(4)	2.246 (2)	Si–C(17)	1.858 (4)
Zr–C(20)	2.485 (3)	Si–C(18)	1.859 (3)
Zr–C(21)	2.503 (4)	Si–C(19)	1.848 (4)
Zr–C(22)	2.520 (4)	C(1)–C(2)	1.371 (3)
Zr–C(23)	2.533 (4)	C(2)–C(3)	1.482 (3)
Zr–C(24)	2.513 (4)	C(2)–C(11)	1.502 (3)
Zr–C(25)	2.527 (3)	C(3)–C(4)	1.359 (3)
Zr–C(26)	2.513 (3)	C(4)–C(5)	1.477 (3)
C(4)–Zr–C(1)	85.5 (1)	C(17)–Si–C(1)	109.7 (2)
C(4)–Zr–D(1)	104.1 (1)	C(2)–C(1)–Si	125.5 (2)
C(1)–Zr–D(2)	106.7 (1)	C(2)–C(1)–Zr	102.2 (2)
D(3)–Zr–D(2)	113.4 (1)	Si–C(1)–Zr	132.3 (1)
D(3)–Zr–D(1)	110.6 (1)	C(11)–C(2)–C(3)	113.0 (2)
D(2)–Zr–D(1)	136.0 (1)	C(11)–C(2)–C(1)	122.3 (2)
C(19)–Si–C(18)	108.5 (2)	C(3)–C(2)–C(1)	124.7 (2)
C(19)–Si–C(17)	105.6 (2)	C(4)–C(3)–C(2)	125.3 (2)
C(19)–Si–C(1)	111.4 (2)	C(5)–C(4)–C(3)	122.3 (2)
C(18)–Si–C(17)	104.8 (2)	C(5)–C(4)–Zr	135.5 (2)
C(18)–Si–C(1)	116.1 (1)	C(3)–C(4)–Zr	102.2 (2)

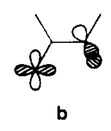
Table IV. Atomic Fractional Coordinates and Equivalent Isotropic Thermal Parameters ($Å^2$), with Standard Deviations in Parentheses, of 3c[a]

atom	x	y	z	U_{eq}
Zr	0.1641 (1)	0.0584 (1)	0.2553 (1)	0.033
Si	0.2637 (1)	−0.1128 (1)	0.3254 (1)	0.053
C(1)	0.1361 (3)	−0.0494 (1)	0.2587 (1)	0.037
C(2)	−0.0074 (3)	−0.0599 (1)	0.1954 (1)	0.034
C(3)	−0.1124 (3)	−0.0083 (1)	0.1452 (2)	0.037
C(4)	−0.0783 (3)	0.0560 (1)	0.1531 (1)	0.032
C(5)	−0.1887 (3)	0.1047 (1)	0.1004 (1)	0.034
C(6)	−0.3289 (3)	0.0896 (1)	0.0344 (2)	0.043
C(7)	−0.4283 (4)	0.1377 (2)	−0.0133 (2)	0.054
C(8)	−0.3894 (4)	0.2019 (2)	0.0038 (2)	0.058
C(9)	−0.2521 (4)	0.2182 (1)	0.0687 (2)	0.058
C(10)	−0.1526 (4)	0.1701 (1)	0.1163 (2)	0.046
C(11)	−0.0724 (3)	−0.1266 (1)	0.1692 (1)	0.035
C(12)	−0.1686 (4)	−0.1621 (1)	0.2190 (2)	0.051
C(13)	−0.2204 (4)	−0.2246 (1)	0.1950 (2)	0.056
C(14)	−0.1818 (4)	−0.2519 (1)	0.1216 (2)	0.051
C(15)	−0.0907 (4)	−0.2164 (1)	0.0704 (2)	0.052
C(16)	−0.0370 (4)	−0.1541 (1)	0.0934 (2)	0.047
C(17)	0.4809 (6)	−0.0804 (2)	0.3750 (3)	0.102
C(18)	0.3115 (5)	−0.1868 (2)	0.2661 (2)	0.076
C(19)	0.1597 (7)	−0.1372 (2)	0.4183 (2)	0.105
C(20)	0.4772 (4)	0.0641 (2)	0.2433 (3)	0.078
C(21)	0.4019 (5)	0.0239 (2)	0.1763 (3)	0.076
C(22)	0.2893 (5)	0.0604 (2)	0.1166 (2)	0.070
C(23)	0.2962 (4)	0.1231 (2)	0.1451 (2)	0.069
C(24)	0.4116 (5)	0.1265 (2)	0.2228 (3)	0.074
C(25)	−0.0121 (5)	0.0520 (1)	0.3768 (2)	0.061
C(26)	−0.0545 (4)	0.1106 (2)	0.3342 (2)	0.055
C(27)	0.0925 (5)	0.1494 (1)	0.3490 (2)	0.060
C(28)	0.2266 (5)	0.1152 (2)	0.4007 (2)	0.075
C(29)	0.1602 (6)	0.0542 (2)	0.4184 (2)	0.072

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*\bar{a}_i\cdot\bar{a}_j$



a



b

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(19) See however: McDade, C.; Bercaw, J. E. *J. Organomet. Chem.* **1985**, *279*, 281 and references therein.

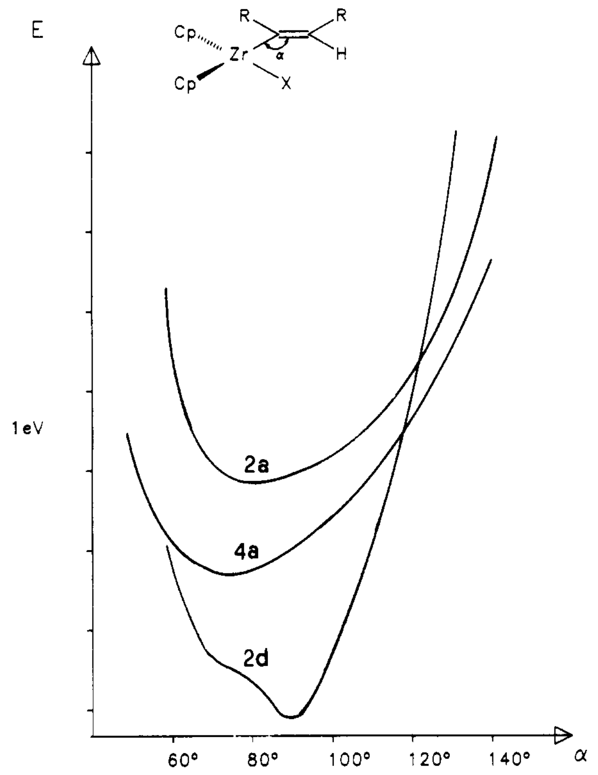

Figure 3. Total energy curves of **2a**, **2d**, and **4a** as a function of α. Each curve is referred to an arbitrary zero of energy. Thus, there is no interrelation in absolute energy between the curves.

the extended Hückel method.[20] In both cases we find a global minimum for $\alpha = 88.2°$ and $\beta = 110°$ (**2d**) and $\alpha = 74.6°$ and $\beta = 110°$ (**4a**), respectively. No local minima were detected. In Figure 3 the potential energy curves as a function of α are compared for **2a**, **2d**, and **4a**. In all three cases we notice a sizable decrease of α from 120°.

This reduction can be rationalized by electronic effects. The bonding interaction between the C(2)–H σ-bond and the empty d_σ MO leads to an additional stabilization[16a,21] of the molecule, which outweighs the repulsion between H and Zr and the bending of the Zr–C(1)–C(2) angle. The electronic interaction is shown schematically above in structure b. In Table V we list the calculated values for α of **2a**, **2d**, and **4a**. Together with these values we give the energy change, ΔE, as well as the change of the net charge, Δq, for the hydrogen atom at C(2) and the metal center, when α is reduced from 120 to 90°. As anticipated from our previous studies,[4b] we encounter a transfer of electron density from the hydrogen atom at C(2) to the metal. In Table V we also show the values calculated for α, ΔE, and Δq for $Cp_2Zr(Cl)C(CH_3){=}CHZr(Cl)Cp_2$ (**8**) and the parent compound $Cp_2Zr(Cl)CH{=}CH_2$ (**9**). We also find agostic interactions for **8** but none for **9**. This is expected, because in all compounds except **9**, the vinylic skeleton is loaded with large substituents that force the C(2)–H atom close to the metal. We encounter the largest stabilization (see Table V) by agostic interactions for the possible intermediates **2d** and **4a**. In view of the predicted close proximity of the positively charged hydrogen atom at C(2) and the negatively charged Cl atom in **2d** or the hydride center in **4a**, it seems reasonable that HCl or H_2 is split off from **2d** or **4a**, respectively, to yield a coordinatively unsaturated (alkyne)zirconocene derivative such as **6a**.

Table V. Calculated Values for α, the Energy Difference ΔE, and the Change of the Net Charge Δq for the H Bound to C(2) and for the Zr Atom[a]

compd	α, deg	ΔE, kcal/mol	Δq H	Δq Zr
$Cp_2ZrCl[CSiMe_3{=}CHPh]$ (**2a**)	83	23.5	+0.08	−0.13
$Cp_2ZrCl[CPh{=}CHPh]$ (**2d**)	88.2	90.9	+0.08	−0.14
$Cp_2ZrH[CSiMe_3{=}CHPh]$ (**4a**)	74.6	35.4	+0.08	−0.20
$Cp_2ZrCl[CMe{=}CH]ZrClCp_2$ (**8**)	94	13.0	+0.06	−0.15
$Cp_2ZrCl[CH{=}CH_2]$ (**9**)	120	−4.1	+0.02	−0.04

[a] $\Delta E = E(\alpha = 120°) - E(\alpha = 90°)$; $\Delta q = q(\alpha = 120°) - q(\alpha = 90°)$.

Conclusions

We have seen several reactions of the alkenylzirconocene complex **2a** that proceed with cleavage of a C–H bond at the β-position of the σ-alkenyl ligand. Since similar alkenylmetallocene derivatives lacking the β-CH agostic interaction found in **2a** react by completely different reaction paths,[19] we have reason to believe that the reactions described above typically involve specific features of the agostic =CR—H—Zr bond. The described formation of (alkyne)zirconocene complexes via elimination of dihydrogen from $Cp_2Zr(H)C(SiMe_3){=}CPhH$ or an additional alkyne ligand from $Cp_2Zr(C{\equiv}CR)C(SiMe_3){=}CPhH$, respectively, has the characteristics of an acid–base reaction. It seems that for these examples agostic activation makes the alkenyl β-hydrogen indeed more acidic.[9]

It has been noted by us and others that hydrozirconation reactions of certain alkynes, bearing bulky substituents, sometimes takes an anomalous course.[4a,22] Metallacyclopentadienes are formed with loss of hydrogen instead of the usual alkenylzirconocene addition products. The clean formation of the metallacycle **3d** by hydrozirconation of tolan at room temperature is a typical example (see Scheme III). In view of our model calculations it is quite likely that β-CH agostic alkenylzirconocene complexes such as **2d** and **4d** are formed along the reaction course. Since complex **4d** is also expected to be formed by addition of zirconocene dihydride to acetylene, this variant of the anomalous hydrozirconation might be taking place via agostic alkenylmetallocene intermediates as well. Investigations aimed at positively distinguishing between the published mechanistic schemes[22] for this reaction type from our proposal on an experimental basis are currently being pursued in our laboratory.

Experimental Section

Reactions with organometallic compounds were carried out under argon with use of Schlenk-type glassware. Solvents were dried with potassium–benzophenone, P_4O_{10}, or lithium aluminum hydride and distilled under argon prior to use. Benzene-d_6 and toluene-d_8 were dried with sodium–potassium alloy; $CDCl_3$ was dried with Sicapent (Merck) and distilled under argon. The following spectrometers were used: Bruker WP 200 SY (^1H, 200 MHz; ^{13}C, 50 MHz) NMR spectrometer, Nicolet 5 DXC FT IR spectrometer. Elemental analyses were carried out at the Institut für Anorganische Chemie der Universität Würzburg and Dornis

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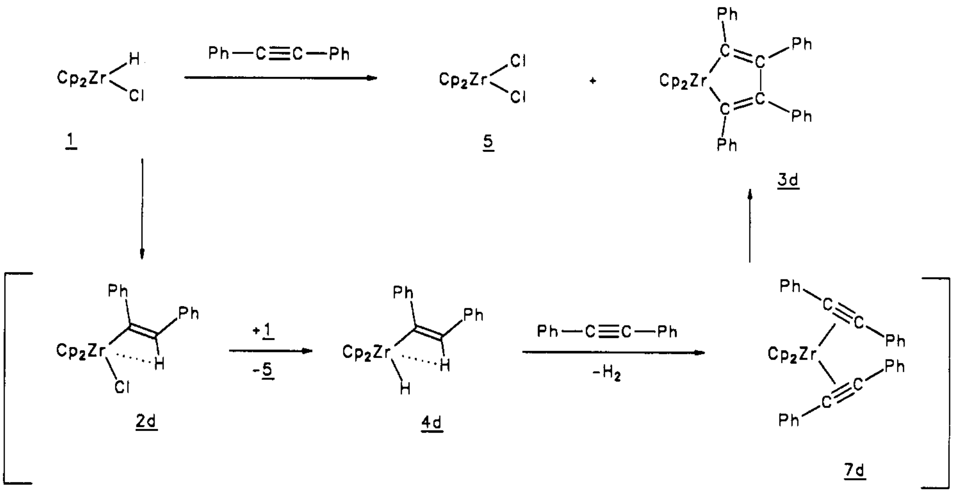
Scheme III



and Kolbe, Mikroanalytisches Laboratorium, Mülheim a. d. Ruhr, FRG. Melting points are uncorrected. The hydrozirconation reagent $[Cp_2Zr(H)Cl]_x$ was prepared according to a literature procedure.[23] The hydrozirconation of $Me_3SiC{\equiv}CPh$ to give a mixture of the products **2a**, **5**, and **3a** has been described previously,[4a] as have general procedures used for our model calculations.

Photolysis of $Cp_2Zr(Cl)C(SiMe_3){=}CPhH$ (2a). A sample of 0.51 g of the product mixture obtained by hydrozirconation of $Me_3SiC{\equiv}CPh$ in 10 mL of toluene is irradiated for 5 h at 0 °C (HPK 125, Pyrex filter). During the photolysis a yellow solid precipitates. It is collected by filtration and dried in vacuo to give 0.32 g (18% from **2a**) of 1,1-bis(cyclopentadienyl)-2,5-bis(trimethylsilyl)-3,4-diphenyl-1-zirconacyclopentadiene (**3a**), mp 124–126 °C dec. Anal. Calcd for $C_{32}H_{38}Si_2Zr$: C, 67.42; H, 6.71. Found: C, 67.59; H, 6.83. ^1H NMR (benzene-d_6): δ −0.17 (s, 18 H, $SiMe_3$), 6.15 (s, 10 H, Cp), 6.65–6.95 (m, 10 H, Ph). ^{13}C NMR (benzene-d_6): δ 2.9 (q, $^1J_{CH}$ = 118 Hz, $SiMe_3$), 111.4 (d, $^1J_{CH}$ = 172 (Hz, Cp), 125.0 (d, $^1J_{CH}$ = 161 Hz, Ph), 126.8 (d, $^1J_{CH}$ = 161 Hz, Ph), 130.0 (d, $^1J_{CH}$ = 160 Hz, Ph), 146.0 (s), 150.1 (s), 204.6 (s, C^α). Crystals of **3a** suitable for X-ray diffraction were obtained from pentane.

X-ray crystal structure analysis of $C_{32}H_{38}Si_2Zr$ (3a): M_r = 570.1; crystal size (mm) 0.47 × 0.16 × 0.50; monoclinic, space group $C2/c$; a = 21.241 (4) Å, b = 10.881 (2) Å, c = 14.692 (3) Å, β = 116.91 (1)°; V = 3028 Å^3; Z = 4; d_{calcd} = 1.25 g cm^{-3}; μ(Mo Kα) = 4.51 cm^{-1}; $F(000)$ = 1192; data collected on an Enraf-Nonius CAD-4 diffractometer; radiation Mo Kα (graphite monochromated), λ = 0.71069 Å; scan mode θ–2θ; T = 20 °C; $[(\sin\theta)/\lambda]_{max}$ = 0.65; measured reflections ($\pm h,+k,+l$) 6822; independent reflections 3416; observed reflections ($I > 2\ \sigma(I)$) 2674 for 159 refined parameters; structure solved by heavy-atom method; hydrogen atom positions located and kept fixed in the final refinement stages; R = 0.035; R_w = 0.039 ($w = 1/\sigma^2(F_o)$); GOF = 1.85; residual electron density 0.34 e Å^{-3}.

Reaction of 2a with Benzylmagnesium Bromide. A solution of benzylmagnesium bromide (4.50 mmol) in 3.0 mL of ether is added to 1.94 g (4.50 mmol) of (E)-(2-phenyl-1-(trimethylsilyl)-ethenyl)zirconocene chloride (**2a**) in 20 mL of toluene. The mixture is stirred for 18 h at 20 °C. The solution is then concentrated in vacuo to a volume of 15 mL and filtered. The clear red filtrate is concentrated in vacuo to 2 mL. Then 10 mL of pentane is added. The resulting precipitate is recovered by filtration, washed three times with 2-mL portions of pentane, and then dried in vacuo to give 1.3 g (61%) of $Cp_2Zr(Br)C(SiMe_3){=}CPhH$, identified by comparison with an authentic sample.

Hydrozirconation of Tolan. Hydridozirconocene chloride (1.40 g, 5.43 mmol) and 0.96 g (5.39 mmol) of diphenylacetylene are stirred in 20 mL of toluene for 24 h at 18 °C. The suspension is filtered. The resulting clear red solution is concentrated in vacuo to a volume of 5 mL. Pentane (20 mL) is added. The orange precipitate is recovered by filtration and dried in vacuo. One obtains 1.70 g of an orange solid that according to the NMR analysis consists of equal molar amounts of Cp_2ZrCl_2 (**5**) and $Cp_2ZrCPh{=}CPhCPh{=}CPh$ (**3d**). ^1H NMR (benzene-d_6): δ 6.00 (s, 10 H, Cp), 6.65–7.10 (m, 20 H, Ph). ^{13}C NMR (chloroform-d): δ 111.9 (d, Cp), 122.7, 124.2, 126.3, 127.1, 127.4, 130.7 (each d, Ph), 141.1 (s), 141.9 (s), 147.8 (s), 194.0 (s, C^α).

1,1-Bis(cyclopentadienyl)-3,5-diphenyl-2-(trimethylsilyl)-1-zirconacyclopentadiene (3c). A sample of 0.63 g (1.46 mmol) of (E)-(2-phenyl-1-(trimethylsilyl)ethenyl)zirconocene chloride (**2a**) and 0.50 g (4.63 mmol) of phenyl lithioacetylenide in 40 mL of diethyl ether is stirred for 18 h at 18 °C. The mixture turns orange. Ether is removed in vacuo. The residue is extracted with 20 mL of toluene and filtered. Solvent is removed from the filtrate in vacuo. Hexane (10 mL) is added with stirring to give a yellow solid, which is recovered by filtration and dried in vacuo to give 0.43 g (59%) of **3c**. Anal. Calcd for $C_{29}H_{30}SiZr$: C, 69.96; H, 6.07. Found: C, 69.71; H, 6.31. Mp: 176–177 °C. ^1H NMR (benzene-d_6): δ −0.05 (s, 9 H, $SiMe_3$), 5.97 (s, 10 H, Cp), 6.92–7.22 (m, 11 H, =CH– and Ph). ^{13}C NMR (benzene-d_6): δ 2.7 (q, $^1J_{CH}$ = 118 Hz, $SiMe_3$), 110.5 (d, $^1J_{CH}$ = 172 Hz, Cp), 121.5 (d, $^1J_{CH}$ = 149 Hz, =CH–), 126.2, 126.3, 126.9, 127.8, 128.1, 128.4 (each d, Ph), 143.5 (s), 147.5 (s), 151.0 (s), 192.9 (s), 197.8 (s). Crystals of **3c** suitable for the X-ray structural analysis were obtained from toluene.

X-ray crystal structure analysis of $C_{29}H_{30}SiZr$ (3c): M_r = 497.9; crystal size (mm) 0.36 × 0.43 × 0.50; monoclinic, space group $P2_1/n$; a = 7.798 (1) Å, b = 20.695 (2) Å, c = 15.549 (2) Å, β = 100.15 (1)°; V = 2470 Å^3; Z = 4; d_{calcd} = 1.34 g cm^{-3}; μ(Mo Kα) = 4.97 cm^{-1}; $F(000)$ = 1032; data collected on an Enraf-Nonius CAD-4 diffractometer; radiation Mo Kα (graphite monochromated), λ = 0.71069 Å; scan mode θ–2θ; T = 20 °C; $[(\sin\theta)/\lambda]_{max}$ = 0.65; measured reflections ($\pm h,+k,$+l) 5973; independent reflections 5615; observed reflections ($I > 2\sigma(I)$) 4794 for 280 refined parameters; structure solved by heavy-atom method; hydrogen atom positions located and kept fixed in the final refinement stages; R = 0.035; R_w = 0.047 ($w = 1/\sigma^2(F_o)$); GOF = 2.65; residual electron density 0.74 e Å^{-3} (near Zr).

1,1-Bis(cyclopentadienyl)-5-methyl-3-phenyl-2-(trimethylsilyl)-1-zirconacyclopentadiene (3b). A mixture of 0.96 g (2.22 mmol) of **2a** and 0.40 g (8.70 mmol) of propynyllithium in 40 mL of ether is stirred for 40 h at 20 °C. Solvent is then removed in vacuo. Toluene (10 mL) is added. The mixture is filtered; the filtrate is then concentrated in vacuo to a volume of 1 mL. At −78 °C a 5-mL portion of hexane is added with stirring. The precipitate is recovered by filtration while still cold to give 0.54 g (56%) of **3b**. Anal. Calcd for $C_{24}H_{28}SiZr$: C 66.15; H, 6.48. Found: C, 66.29; H, 6.40. Mp: 113–114 °C. ^1H NMR (benzene-d_6): δ −0.06 (s, 9 H, $SiMe_3$), 2.00 (d, $^4J_{HH}$ = 1.6 Hz, 3 H, CH_3), 5.90 (s, 10 H, Cp), 6.30 (q, $^4J_{HH}$ = 1.6 Hz, 1 H, =CH–), 7.05–7.20 (m, 5 H, Ph). ^{13}C NMR (benzene-d_6): δ 2.7 (q, $^1J_{CH}$

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= 119 Hz, $SiMe_3$), 29.3 (q, $^1J_{CH}$ = 124 Hz, CH_3), 110.2 (d, $^1J_{CH}$ = 173 Hz, Cp), 122.4 (d, $^1J_{CH}$ = 148 Hz, =CH–), 126.0, 127.6, 128.0 (each d, Ph), 145.1 (s), 151.0 (s), 191.8 (s), 199.3 (s).

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Supplementary Material Available: Details on the X-ray data collection and structure determination of **3a** and **3c** and lists of bond lengths and angles, atomic fractional coordinates, and thermal parameters of **3a** and **3c** (13 pages); listings of observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

Communications

Phase-Transfer-Catalyzed P–C Bond Cleavage in Platinum Bis(diphenylphosphino)methane Complexes under Exceedingly Mild Conditions

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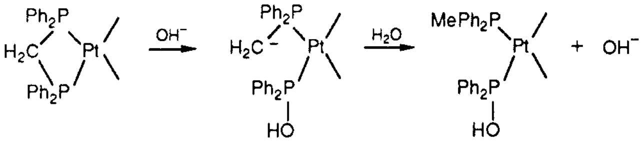
Summary: The reaction of [Pt(dppm)Cl_2] (dppm = $Ph_2PCH_2PPh_2$) with [S(O)Me_3]Cl under basic phase-transfer-catalyzed conditions gave the complex {Pt(PPh_2Me)[PPh_2(OH)][$(CH_2)_2$S(O)Me]}Cl, which contains a bidentate sulfur ylide and two monodentate phosphine ligands. The latter was produced by the facile base hydrolysis of the dppm ligand, a reaction that is general for other Pt–dppm complexes.

In recent years, there has been increasing interest in the use of phase-transfer catalysis (PTC) in organometallic chemistry.[1] We have previously shown that sulfur ylide complexes of palladium could be prepared using the biphasic PTC/OH^- technique.[2] We have further pointed out that sulfur ylide complexes of palladium could be prepared even in water under basic conditions.[3] While continuing our efforts to synthesize sulfur ylide complexes of platinum, we have discovered a novel phase-transfer-catalyzed P–C bond cleavage reaction in Pt–dppm (dppm = $Ph_2PCH_2PPh_2$) complexes. Dppm has usually been used as a bridging ligand for binuclear or cluster complexes. Although it has been thought to be relatively inert under normal conditions, reports on the reaction of coordinated dppm have appeared.[4] The major reactions are deprotonation of the coordinated dppm and the reaction of the deprotonated dppm with electrophiles.[4] This paper reports the first example of the facile base hydrolysis of a dppm ligand in a Pt–dppm complex to a PPh_2Me and PPh_2(OH) ligand. This phase-transfer-catalyzed reaction takes place under exceedingly mild conditions (room temperature, <2 N NaOH solution, normal PTC conditions).

Scheme I



Treatment of Pt(dppm)Cl_2 in CH_2Cl_2 with [S(O)Me_3]Cl in NaOH using n-Bu_4NCl as the phase-transfer catalyst gave a pale yellow compound, **1**,[5] in 85% yield. Other catalysts such as 15-crown-5 ether and n-$C_{16}H_{33}N(CH_3)_3Br$ work equally well. In the absence of a PT catalyst, results are varied, but normally the reaction is slow and side products are obtained. In this PT-catalyzed reaction, the dppm in the platinum compound was hydrolyzed, and a chelated sulfur ylide was formed. Addition of NH_4PF_6 to the ethanol solution of **1** gave a light yellow precipitate, **2**[6] (94% yield), which has PF_6 as a counteranion. The ^{31}P NMR spectrum of **1** indicates that there are two nonequivalent phosphorus atoms in a cis configuration—the upfield signal (2.4 ppm) is assigned to the coordinated PPh_2Me, while the downfield signal (51.5 ppm) is due to coordinated PPh_2(OH). The ^1H NMR spectrum of **1** shows the presence of a coordinated PPh_2Me (δ = 1.89, 1:1:4:4:1:1 multiplet).[7] The position and relative intensity of the P–OH proton are less obvious due to the proton exchange between P–OH and H_2O present in the $CDCl_3$. The IR spectrum of **1** reveals the presence of an O–H stretching band at 3380 cm^{-1}. The molar conductance of **1** in acetone (15 Ω^{-1} cm^2 mol^{-1}) is lower than the values expected for a 1:1 electrolyte. Although compound **2** differs from **1** only

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[5] Compound **1**: mp 157–159 °C; IR (KBr) ν(OH) 3380, ν(SO) 1180 cm^{-1}; Λ_M = 15 Ω^{-1} cm^2 mol^{-1}; ^1H NMR ($CDCl_3$) 7.2–7.7 (m), 3.09 (t, J(H,H) = 1.8 Hz), 2.1–2.4 (m), 1.89 (m, J(P,H) = 10 Hz, J(Pt,H) = 25.7 Hz) ppm; ^{31}P NMR ($CDCl_3$) 51.5 (m, J(P,P) = 24.4 Hz, J(Pt,P) = 3215.5 Hz), 2.4 (m, J(P,P) = 24.4 Hz, J(Pt,P) = 2948.5 Hz) ppm, downfield relative to 85% H_3PO_4. Anal. Calcd for $C_{28}H_{31}ClO_2P_2SPt$: C, 46.4; H, 4.3. Found: C, 46.3; H, 4.5.

[6] Compound **2**: mp 120 °C (dec); IR (KBr) ν(OH) 3380, ν(SO) 1180 cm^{-1}; Λ_M = 67 Ω^{-1} cm^2 mol^{-1}; ^1H NMR ($CDCl_3$) 7.2–7.7 (m), 3.1 (t, J(H,H) = 1.8 Hz), 2.1–2.4 (m), 1.85 (m, J(P,H) = 10 Hz, J(Pt,H) = 25.7 Hz) ppm; ^{31}P NMR ($CDCl_3$) 67.9 (m, J(P,P) = 24.9 Hz, J(Pt,P) = 3245.1 Hz), 2.3 (m, J(P,P) = 24.9 Hz, J(Pt,P) = 2853.6 Hz), –143 (sept, J(P,F) = 706.2 Hz) ppm. Anal. Calcd for $C_{28}H_{31}F_6O_2P_3SPt$: C, 40.4; H, 3.7. Found: C, 40.2; H, 3.5.

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