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Synthesis of group 4 metallocene-substituted ylides and their reaction with ketones

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Abstract

A new method has been developed to synthezise group 4 metallocene ylides. $Ph_3P{=}CH_2$ reacts with in situ generated (η^2-ethene)MCp_2 (M = Zr, Hf), (η^2-aryne)MCp_2 (M = Ti, Zr), or with (η^4-conjugated diene)MCp_2 (M = Zr, Hf) via intramolecular hydrogen transfer to form metallocene ylides $Cp_2M(R)CH{=}PPh_3$. In some cases competitive methylene transfer occurs leading to four-membered metallacycles. The metallocene ylides all exhibit a substantial metal to carbon π-interaction, increasing in strength on going from hafnium to titanium as the central metal atom. Ylide reactivity is greatly reduced. With a non-enolizable ketone, $Cp_2Zr(CH_2CH{=}CHCH_3)CH{=}PPh_3$ reacts via the reverse of the metallocene ylide forming reaction. With enolizable ketones, zirconocene or hafnocene ylides serve as bases and form metal enolates. The resulting enolate (*E*)/(*Z*) ratio strongly depends on the group R of the metallocene ylide base $Cp_2Zr(R)CH{=}PPh_3$.

The chemistry of ylides is markedly dependent on the nature of the substituents at the ylide carbon. Traditionally, a wide range of organic functional groups R has been used to modify synthetically useful ylides, e.g. $RCH{=}PPh_3$ (1) [1]. However, organometallic substituents should in principle have an even greater potential for controlling ylide reactivity and structural features [2].

Directly bonded metal complex fragments could interact with an ylide carbon center in two ways. The general metal σ-donor properties ($+I$ effect) would induce an increased electron density at carbon and thereby probably enhance the ylide nucleophilicity [3 *].

This effect would make the $MCH{=}PPh_3$ species **2** a more reactive reagent in typical ylide reactions, like the Wittig carbonyl olefination, as compared to **1**.

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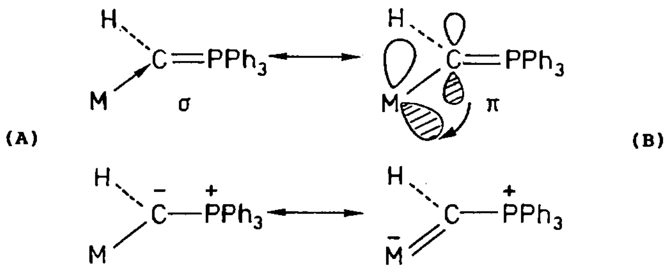


Scheme 1

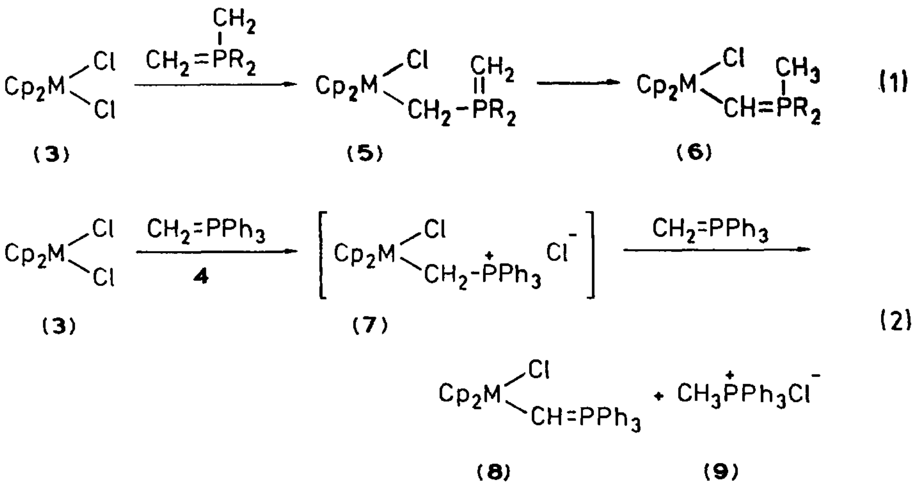
However, for a variety of metal complex fragments an opposing effect has to be taken into account. Main group metals as well as transition metal complexes possessing suitable acceptor orbitals may interact with the filled carbon centered *p*-orbital [4] of the ylide moiety. The resulting carbon to metal π-back donation (possibly creating a partial metal-to-carbon double bond, as depicted in Scheme 1) would decrease the electron density at carbon and thus lead to a reduced ylide nucleophilicity of **2**.

Formally d^0-configurated bent metallocene units $Cp_2M(X)$ of the group 4 transition metals titanium, zirconium, and hafnium are especially interesting organometallic substituents in this respect. According to their position in the periodic table these metals are reasonably strong σ-donors. At the same time, the chances are good that the special stereoelectronic properties of the 16-electron bent metallocene fragments [5] in $Cp_2M(X)CH{=}PPh_3$ complexes ("metallocene ylides"; M = Ti, Zr, Hf) facilitate the formation of a substantial carbon to metal π-interaction, thereby reducing electron density at the ylide carbon.

The relative contribution of these two opposing effects will certainly depend on the nature of the metal center as well as its surrounding ligands. In order to understand better the relative importance of these electronic influences of the $Cp_2M(X)$ fragment on the ylide carbon center for a given metal/ligand combination we have prepared a variety of new examples of metallocene ylides **2**, examined their structural and spectroscopic features, and investigated their reactivity towards several organic carbonyl compounds [6 *].

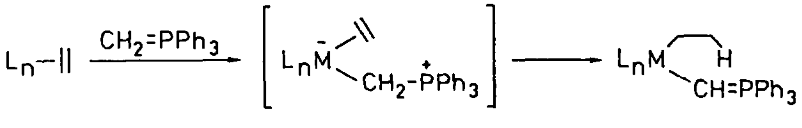
Preparation of metallocene ylides

Metallocene ylides have been prepared via different variants of the "trans-ylidation" reaction [7]. A route developed by Schmidbaur et al. [8] employed the facile metathesis reaction of a metal halide with readily available (methylene)dialkyl (or diamino)phosphinomethylides followed by a rapid intramolecular trans-ylidation reaction. A variety of metal substituted ylides $L_nMCH{=}P(Me)R_2$ bearing at least one methyl group at phosphorus have become available by this elegant synthetic route (Scheme 2, reaction sequence 1) [9]. Kaska et al. have shown that metallocene ylides can be prepared similarly by making use of an intermolecular trans-ylidation reaction between a metallocene phosphonium salt **7** (generated in situ from Cp_2MCl_2 (M = Zr, Hf) (**3**) and $CH_2{=}PPh_3$ (**1a**)) and excess methylene triphenylphosphorane (Scheme 2, reaction sequence 2) [10].



Scheme 2

For this study we have prepared metallocene ylides by a rather different route. Our novel synthetic entry to this class of compounds makes use of the high reactivity of a variety of (alkene)metallocene complexes of titanium, zirconium, and hafnium [11 *]. The rather simple general reaction sequence used here is outlined in equation 3. The metallocene ylide is basically formed in a two step reaction sequence. In the first step a coordinatively unsaturated (olefin)metallocene complex (in most cases generated in situ from easily available precursors) is allowed to react with the ylide methylene triphenylphosphorane. We assume that a 1/1 addition product **11** is formed. For the examples reported here this cannot be observed or isolated, however. The reactive intermediate is stabilized by a rapidly occurring subsequent hydrogen migration from the ylide carbon atom to the π-bonded olefinic ligand yielding an alkyl substituted metallocene ylide **8'**.



(3)

(10) (11) (8')

As a first example of this route to metallocene ylides we have recently described the formation of $Cp_2Zr(OCHPh_2)CH{=}PPh_3$ (**8a**) [12] from (η^2-benzophenone)zirconocene dimer [13] and $CH_2{=}PPh_3$. The reaction takes place readily at elevated temperature and produces very pure **8a** in about 50% isolated yield. So far a clean reaction has only been achieved by using the unsubstituted parent ylide methylene triphenylphosphorane. However, our new metallocene ylide synthesis has turned out to be rather widely applicable with regard to the organometallic component.

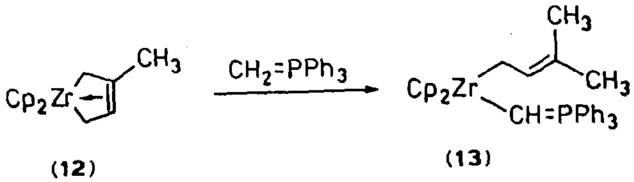
We have successfully used (η^2-ethylene)-hafnocene and -zirconocene (thermally generated from the dicyclopentadienylmetallacyclopentanes) [14], (η^2-aryne)-titanocene and -zirconocene (thermally generated from the corresponding diaryl metallocenes) [15 *] and even (conjugated diene)MCp$_2$ complexes (M = Zr, Hf) [16] as reactive organometallic hydrogen abstracting reagents for the synthesis of Cp$_2$M(R)CH=PPh$_3$ complexes.

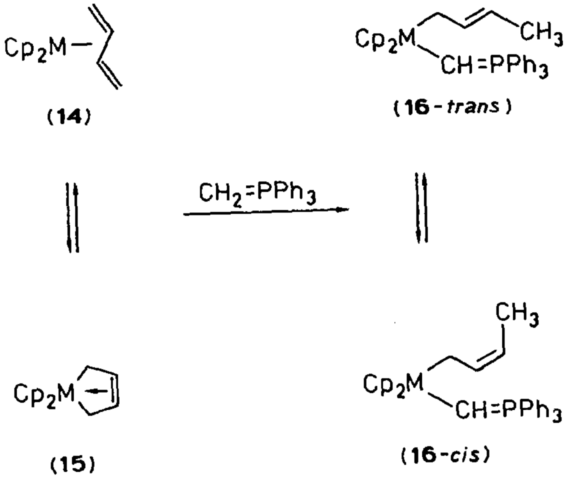
(*s*-*cis*-η^4-Isoprene)zirconocene (**12**) reacts with CH$_2$=PPh$_3$ at room temperature to form the 1/1 addition product **13** [17]. According to the spectroscopic analysis **13** contains a σ-3,3-dimethylallyl moiety at zirconium. In addition, the presence of the metal-substituted ylide unit MCH=PPh$_3$ was clearly identified. Apparently, addition of methylene triphenylphosphorane to the zirconium diene complex has produced a reactive 1/1 adduct which allowed rapid intramolecular transfer of a hydrogen atom from the ylide carbon to a terminal carbon center of the conjugated diene ligand. It has been argued [17] that this facile hydrogen migration reaction might possibly occur in a concerted fashion ascribing this type of organometallic reaction some similarity to the vinylmethylcyclopropane → 1,4-hexadiene rearrangement (i.e. a concerted homo-1,5-hydrogen migration) in a purely organic system [18]. Some support for this view comes from the observed stereochemistry of the analogous reaction of the parent (butadiene)metallocene complexes. (*s*-*trans*-/*s*-*cis*-butadiene)MCp$_2$ mixtures (**14**,**15**; M = Zr (**a**) or Hf (**b**)) react with methylene triphenylphosphorane by transfer of H from the ylide to a terminus of the C$_4$-chain producing σ-crotylmetallocene ylides **16**. These reactions proceed remarkably stereoselectively. On treatment of a mixture of (*s*-*trans*-/*s*-*cis*-C$_4$H$_6$)HfCp$_2$ (75/25) with CH$_2$=PPh$_3$ at −10 °C, the reaction proceeds almost exclusively with the (*s*-*trans*-η^4-butadiene)hafnocene isomer. Under these reaction conditions we observed the stereoselective formation of the *trans*-σ-crotyl-Cp$_2$Hf(C$_4$H$_7$)CH=PPh$_3$ isomer **16b**-*trans*. Rearrangement to the *cis*-σ-crotylhafnocene ylide **16b**-*cis* clearly takes place in a consecutive reaction ($\Delta G^{\ddagger}$(**16b**-*trans* → **16b**-*cis*) = 23.1 ± 0.2 kcal/mol at +34 °C; equil. ratio: **16b**-*trans*/**16b**-*cis* = 57/43 at ambient temperature).

Similar observations have been made for the analogous zirconium system. However, in contrast to **14b**/**15b** it here is exclusively the (*s*-*cis*-η^4-butadiene)ZrCp$_2$ isomer **15a** in the (*trans*/*cis*-diene)metallocene mixture (45/55) that reacts with CH$_2$=PPh$_3$ at −50 °C to form the *trans*-σ-crotylmetallocene ylide product **16a**-*trans* selectively (subsequent *trans* → *cis*-isomerization occurs at significantly higher temperature; $\Delta G^{\ddagger}$(**16a**-*trans* → **16b**-*cis*) = 19.7 ± 0.2 kcal/mol at −20 °C; equil. ratio **16a**-*trans*/**16a**-*cis* = 54/46 at ambient temperature] [17].

(η^2-Ethylene)metallocenes are also suitable precursors for the metallocene ylide synthesis [6b *]. The complexes (η^2-CH$_2$=CH$_2$)MCp$_2$ (M = Zr, Hf) are very reactive and cannot be introduced as such, but have to be generated in situ from the readily available metallacyclopentanes **17** (**a**, M = Zr; **b**, M = Hf) by a thermally induced [2 + 2 + 2] cycloreversion and extrusion of ethylene.

Di-η-cyclopentadienylhafnacyclopentane (**17b**) reacts with methylene triphenylphosphorane at 0 °C exclusively via this reaction path (b, see Scheme 4) to give a ca. 60/40 mixture of the organometallic reaction products **21b** and **22**. We have obtained no evidence for any H transfer occurring from the phosphorus ylide to the C$_4$-chain of the starting material. The isolated products all are formally derived from a reactive ethylenehafnocene species which is presumably being trapped by CH$_2$ = PPh$_3$ to form **20**. Subsequent hydrogen migration then leads to the formation of the metallocene ylide. In a competing reaction the intermediate **20** can also stabilize itself by incorporation of a complete methylene group (with extrusion of the good PPh$_3$ leaving group) to form the metallacyclobutane **22** [19 *].





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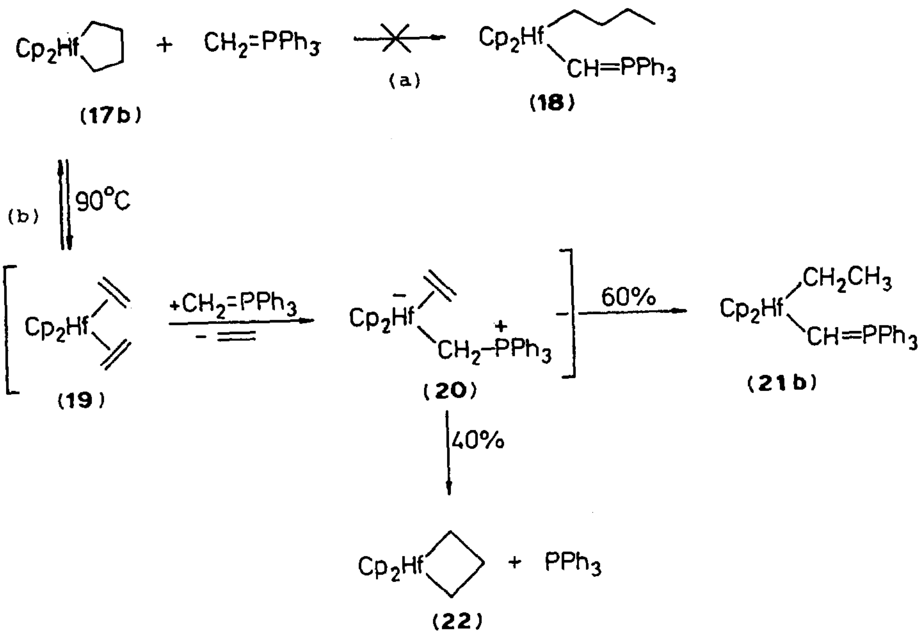
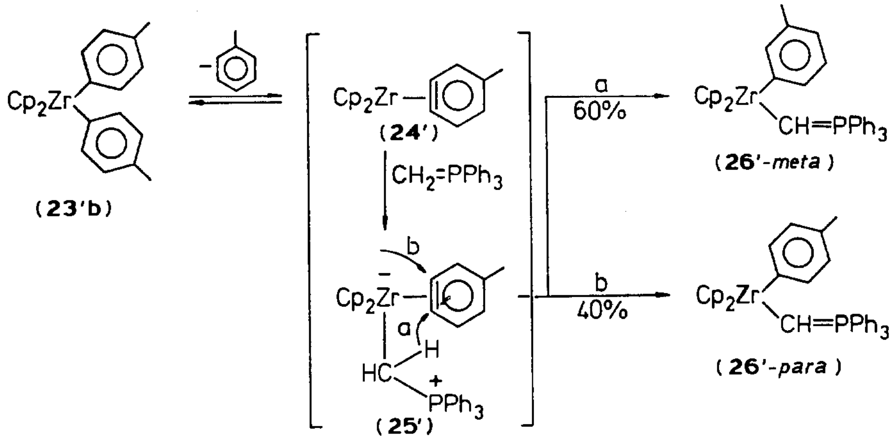
Scheme 3



Scheme 4

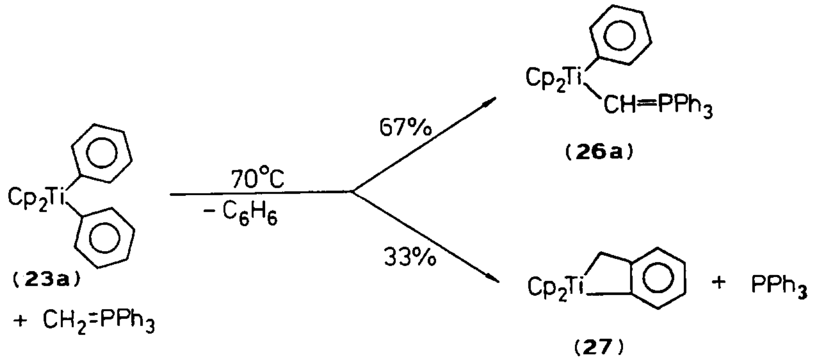


Scheme 5

Di-η-cyclopentadienylzirconacyclopentane (**17a**) is thermally much less stable than the hafnium analogue [14,20], but with $CH_2=PPh_3$ it reacts similarly. At temperatures above 0 °C an equimolar mixture of **17a** and methylenetriphenylphosphorane reacts with ethylene evolution to give the ethylzirconocene ylide $Cp_2Zr(C_2H_5)CH=PPh_3$ (**21a**).

Thermally generated (η^2-aryne)metallocenes react with ylides similarly. Diphenylzirconocene **23b** is unreactive towards $CH_2=PPh_3$ at room temperature. However, at 80 °C (in toluene or heptane solution) it reacts readily with methylenetriphenylphosphorane. One equivalent of benzene is formed. We have isolated the resulting organometallic reaction product $Cp_2Zr(Ph)CH=PPh_3$ (**26b**) in > 90% yield. The formation of an aryne type intermediate was demonstrated by classical labelling experiments [21]. Thermolysis of e.g. (di-*p*-tolyl)zirconocene (**23b'**) generates an unsymmetrically substituted (η^2-aryne)metallocene intermediate **24'**. Trapping of this product by added $CH_2=PPh_3$ yielded a 60/40 mixture of the expected regioisomers **26'b**-*meta* and **26'b**-*para* of the arylzirconocene ylide reaction product.

Cp_2TiPh_2 (**23a**) reacted analogously with $CH_2=PPh_3$ at 70 °C in heptane. In contrast to the zirconium system, the formation of the aryltitanocene ylide again is



(4)

accompanied by a substantial amount of methylene transfer, opening up an interesting synthetic entry to the hitherto unknown di-η-cyclopentadienyltitanacyclobutabenzene ring system, [6c *,22 *]. Both reaction products **26a** and **27** have been shown by labelling experiments to arise from a (η^2-aryne) type intermediate.

Structural features of the metallocene ylides

The alkyl- and aryl-metallocene ylides thus prepared have been characterized spectroscopically and by X-ray crystallography of three representative examples. In the solid state the complexes $Cp_2Hf(C_2H_5)CH{=}PPh_3$ (**21b**), $Cp_2Zr(Ph)CH{=}PPh_3$ (**26b**), and $Cp_2Ti(Ph)CH{=}PPh_3$ (**26a**) all adopt a preferred conformation that allows maximal overlap of the filled p-orbital at the trigonal planar ylide carbon atom with the only available acceptor orbital of the metal center of the bent metallocene unit [5,6 *]. Additional evidence for some degree of ylide-C/M π-interaction arises from a comparison of representative bond distances in compounds **21b**, **26b**, and **26a**. The ylide carbon to hafnium bond in **21b** is somewhat shortened as compared to a "normal" Hf–C(sp^2) bond [23]. Taking the M–C bond of the Cp_2Hf-ethyl moiety in the same molecule as a reference and correcting for the difference in carbon hybridization, it is found that the Hf–C(ylide) linkage in $Cp_2Hf(C_2H_5)CH{=}PPh_3$ (**21b**) is shortened by ca. Δd 0.1 Å as a result of the π-bonding.

A similar comparison of bond distances reveals an even more pronounced metal-to-carbon π-interaction for the phenyl metallocene ylides **26a** and **26b**. For $Cp_2Zr(Ph)CH{=}PPh_3$ (**26b**) a value of Δd 0.18 Å was obtained. For the phenyl titanocene ylide (**26a**) Δd 0.22 Å, indicating an even more pronounced metal-to-carbon π-interaction. Possibly **26a** has to be regarded as already exhibiting a substantial metal carbene type character [24].

An evaluation of what this metal-to-carbon π-interaction might be worth energetically comes from dynamic NMR studies of the metallocene ylides. For most $Cp_2M(R)CH{=}PPh_3$ complexes dynamic NMR spectra have been recorded. Low temperature ^{1}H und ^{13}C NMR spectra reveal a favoured molecular structure analogous to the one observed in the solid state by X-ray diffraction. It is characterized by an arrangement of the $Cp_2MCHPPh_3$ sub-structure that leads to a chemical differentiation of the Cp groups at the bent metallocene unit. From the coalescence of the corresponding NMR resonances of the diastereotopic Cp ligands we have obtained an estimate of the rotational activation barrier of the Cp_2M–C(ylide) bond. The $\Delta G^{\ddagger}_{rot}$ Gibbs activation barriers thus obtained have turned out to be almost invariant to alterations of the σ-hydrocarbyl ligand at Cp_2M. However, we observed a pronounced increase of this rotational activation barrier on changing the central metal atom from hafnium through zirconium to titanium [6 *,17,25].

$Cp_2Hf(C_2H_5)CH{=}PPh_3$ (**21b**) clearly exhibits the lowest M–C(ylide) rotational barrier of the complexes investigated. Splitting of the ^{1}H/^{13}C NMR Cp resonances was observed at low temperatures. However, the rotational process for this compound was too rapid on the NMR time scale (estimated $\Delta G^{\ddagger}_{rot}$ (−140 °C) 8 kcal/mol) to allow low temperature limiting NMR spectra to be recorded [26 *]. In accord with the X-ray crystallographic results the $Cp_2Zr(R)CH{=}PPh_3$ ylides exhibit a somewhat higher rotational barrier. The values obtained for $Cp_2Zr(\sigma\text{-}CH_2CH{=}CHCH_3)CH{=}PPh_3$ (**16a**) ($\Delta G^{\ddagger}_{rot}(T) = 8.3 \pm 0.3$ kcal/mol (−100 °C)) and

$Cp_2Zr(Ph)CH{=}PPh_3$ **26b** (8.4 ± 0.3 (−102°C)) are rather similar to the one reported for $Cp_2Zr(Cl)CH{=}PPh_3$ [10,26 *].

A higher rotational activation barrier is observed for the $Cp_2Ti{-}C$(ylide) linkage in the phenyl titanocene ylide **26a**. The value of $\Delta G^{\ddagger}_{rot}$ (−34°C) = 12.0 + 0.2 kcal/mol obtained from the dynamic ^1H NMR spectra [27] indicates a substantially increased metal-to-carbon π-interaction in solution as compared to the zirconium or hafnium compounds. The gradually changing π-character of the $Cp_2M{-}C$(ylide) bond in a series of metallocene ylides of the group 4 transition metals titanium, zirconium, and hafnium can be followed by consistent alterations of other NMR parameters as well (for selected examples, see Table 1).

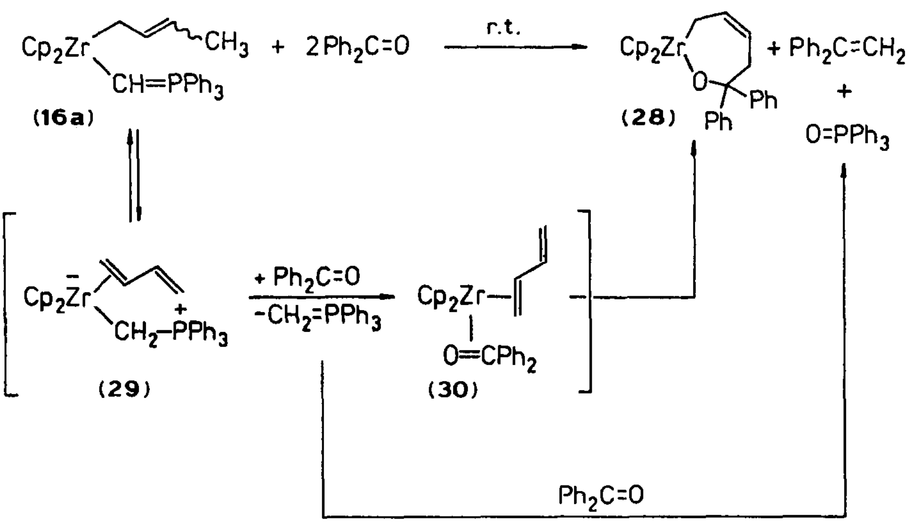
Reactions of metallocene ylides with ketones

The synthetically most useful reaction of phosphorus ylides probably is the Wittig olefination of organic carbonyl compounds. Therefore, it was an interesting question if metallocene ylides could possibly also undergo this reaction despite their pronounced metal-to-carbon π-conjugation interaction.

The equilibrium mixture of σ-crotylzirconocene ylides **16a**-*cis* and -*trans* slowly reacted at room temperature with benzophenone. It took two equivalents of the ketone to achieve a complete conversion of the starting material. A 1/1/1 mixture of three components was formed. The organometallic reaction product was identified as the seven-membered metallacyclic σ-allyl metallocene complex **28**. It formally can be regarded as the coupling product of butadiene and benzophenone at the bent metallocene unit. We had prepared this compound previously by the reaction of (*s-trans*-η^4-butadiene)$ZrCp_2$ with $Ph_2C{=}O$ [28]. The remaining products of the reaction between **16a** and benzophenone were identified as being 1,1-diphenylethene and triphenylphosphine oxide, i.e. the expected products of the Wittig olefination of $Ph_2C{=}O$ with methylene triphenylphosphorane. So obviously, **16a**-*cis*/**16a**-*trans* does not exhibit any ylide reactivity towards the aromatic ketone used but rather undergoes the reverse reaction of its formation. Retro-homo-1,5-hydrogen migration regenerates the butadiene and the $CH_2{=}PPh_3$ system, which both then undergo typical consecutive reactions with the added ketone, the Cp_2Zr(butadiene) moiety undergoing addition with metallacyclic CC coupling. The ylide methylenetriphenylphosphorane set free in this reaction is, of course, not stable in the presence of an organic carbonyl compound. It instantly consumes an additional equivalent of $Ph_2C{=}O$ to form the Wittig products.

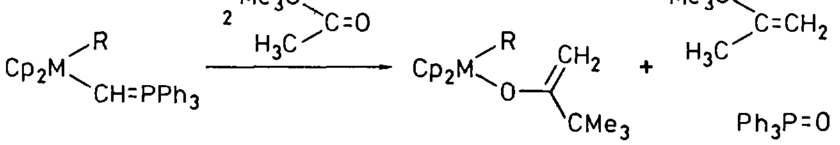
Reactions of metallocene ylides with enolizable ketones take a somewhat different course. However, again two equivalents of the organic carbonyl components are required for a complete reaction. Again, the formation of equimolar amounts of triphenylphosphine oxide and a 1,1-disubstituted ethylene $R^1R^2C{=}CH_2$ indicates the intermediate formation of the Wittig reagent $Ph_3P{=}CH_2$. However, in contrast to the reaction of **16a** with the non-enolizable diaryl ketone (see above) we have obtained no indication of trapping a reactive olefin metallocene intermediate (generated via the reverse of the metallocene ylide forming reaction) by the added ketone [28b]. Instead, the corresponding metallocene enolates [29] are formed in good yields.

Thus, $Cp_2Zr(\sigma\text{-}CH_2CH{=}CMe_2)CH{=}PPh_3$ (**31**) reacts with two molar equivalents of pinacolone (**32**) at ambient temperature to yield the zirconium enolate $Cp_2Zr(\sigma$-



Scheme 6

$CH_2CH=CMe_2)OC(CMe_3)=CH_2$ in addition to the Wittig olefination products $H_2C=CMe(CMe_3)$ and triphenylphosphine oxide.

 (5)

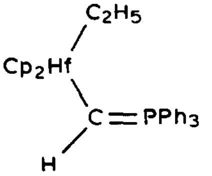
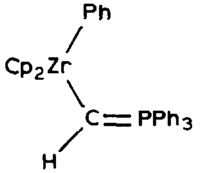
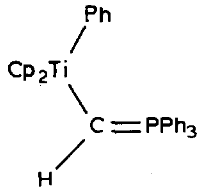
$R = (CH_2\text{-}CH=CMe_2)$, Ph, M = Zr; R = C_2H_5, M = Hf.

Both, $Cp_2Zr(Ph)CH=PPh_3$ (**26b**) and $Cp_2Hf(C_2H_5)CH=PPh_3$ (**16b**) undergo the same type of reaction with the ketone **32**, albeit requiring much more drastic reaction conditions than **31**. At 80 °C/5 h the metallocene enolates $Cp_2Zr(Ph)$-$OCR=CH_2$ (**35b**) and $Cp_2Hf(C_2H_5)OCR=CH_2$ (**33b**, R = t-butyl) are formed in high yield along with the Wittig products $H_2C=CMe(CMe_3)$ and Ph_3PO. Under similar conditions the titanocene ylide $Cp_2Ti(Ph)CH=PPh_3$ (**26a**) does not undergo this reaction. Even prolonged treatment of **26a** with excess methyl t-butyl ketone in refluxing benzene did not result in a measurable consumption of the metallocene ylide. The organometallic starting material was recovered unchanged.

The formation of the metallocene enolates by reaction of the metallocene ylides with excess pinacolone could in principle proceed via two different routes. The ylide carbon of the $Cp_2MCH=PPh_3$ moiety could possess a sufficiently pronounced basic character to directly abstract a proton from the α carbon of the ketone. Alternatively, one might envisage a reaction pathway related to Scheme 6 where the reversal of the metallocene ylide forming reaction generates $Ph_3P=CH_2$ plus a reactive (η^2-alkene)metallocene which then subsequently serves as a hydrogen acceptor from the enolizable ketone.

Labelling experiments using pinacolone-d_3 rapidly ruled out the latter alternative for the metallocene enolate formation starting from $Cp_2Zr(Ph)CH=PPh_3$ (**26b**) or

Table 1
A comparison of selected spectroscopic data and chemical features between metallocene ylides **21b** (Hf), **26b** (Zr), and **26a** (Ti).

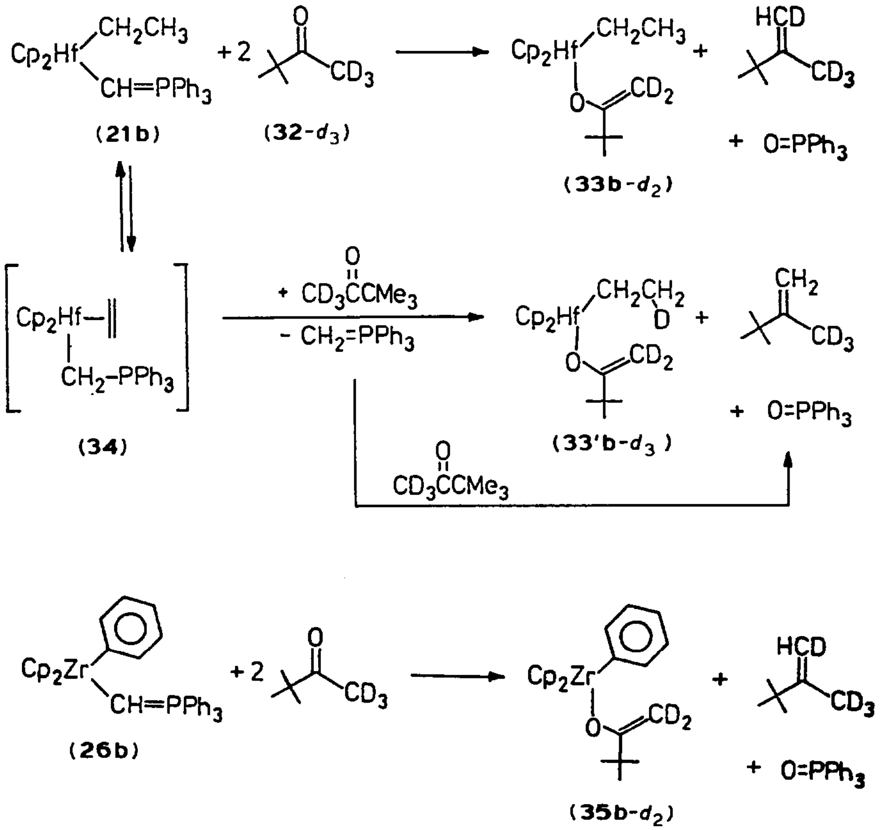
	$^1H/^{13}C$ NMR [a] (Ylid-CH, δ)	Δd (Å)	$\Delta G^{\ddagger}_{rot}$ [b]	Base [c]	Nucl. [c]
	3.72/ 91.6	0.106	< 8	+	–
	5.65/106.2	0.181	8.4	+	–
	8.78/165.2	0.221	12.0	–	–

[a] Compare: $Ph_3P{=}CH_2$ 0.74/–4.2. [b] kcal/mol. [c] Towards $(Me_3C)COCH_3$ at 80 °C.

$Cp_2Hf(C_2H_5)CH{=}PPh_3$ (**21b**). According to Scheme 7 reversible metallocene ylide formation via H-migration starting from **21b** would have revealed itself by incorporation of deuterium in the Hf-bound ethyl group of the enolate product **33b** and the formation of the Wittig olefination product $Me_3CC(CD_3){=}CH_2$. Instead, within the accuracy of a standard $^1H/^{13}C$ NMR analysis we have only observed $Cp_2Hf(C_2H_5)OC(CMe_3){=}CD_2$ plus $Me_3CC(CD_3){=}CHD$ (see Scheme 7). Similarly, the formation of a mixture of $Cp_2Zr(C_6H_5)OC(CMe_3){=}CD_2$ and $Me_3CC(CD_3){=}CHD$ indicated the phenylzirconocene ylide **26b** simply serving as a base in the enolate forming reaction.

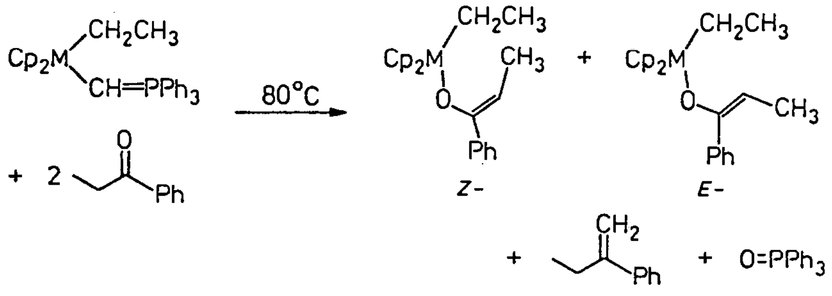
Metal enolates derived from ketones bearing a substituent at the α-carbon serve as very important reagents in aldol type carbon carbon coupling reactions [30]. We therefore tested the ability of the metallocene ylides **21a**, **21b**, and **26b** to serve as bases in the generation of metal enolates from propiophenone. This study disclosed a remarkable influence of the σ-hydrocarbyl ligand at the group 4 metallocene unit on the stereochemistry of the metal enolate formed in this reaction [25,31].

The ethylhafnocene ylide **21b** reacts with propiophenone at 80 °C cleanly to form a mixture of *Z*- and *E*-configurated enolates **36b**. Again two equivalents of the ketone are used to achieve a complete transformation of the starting material. In addition a molar equivalent of each triphenylphosphine oxide and 2-phenyl-1-butene are formed. Under the reaction conditions employed a 87/13 mixture of the



Scheme 7

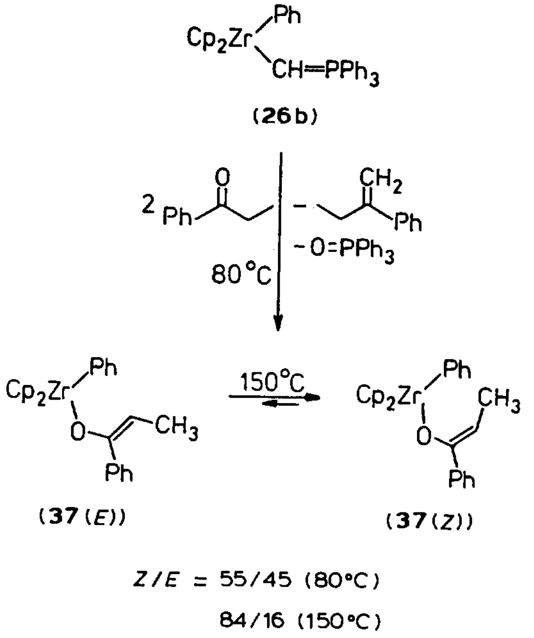
hafnaenolate isomers **36b**(Z) and **36b**(E) was formed. In this case the Z-configurated isomer appears to be the more stable product. Further thermolysis, even at elevated temperature, did not alter the Z/E-ratio. We assume that the obtained mixture thus represents the Z/E-metallaenolate equilibrium situation.



M = Hf (**21b**) **36b**(Z) / **36b**(E) = 87 / 13

M = Hf (**21a**) **36a**(Z) / **36a**(E) = 95 / 5

Scheme 8



Scheme 9

A similar thermodynamic mixture of zirconaenolates was obtained by treating ethylzirconocene ylide **21a** with propiophenone at 80 ° C. The favored formation of the *Z*-configurated metallaenolate here is even more pronounced. A 95/5 mixture of enolates **36a**(*Z*) and **36a**(*E*) was obtained in high yield.

The situation changes drastically if phenylzirconocene ylide **26b** is used as the proton abstracting reagent. Treatment of **26b** with two equivalents of propiophenone at 80 ° C results in the formation of $Ph_3P{=}O$, $CH_2{=}CPhC_2H_5$, and a 55/45 mixture of the zirconaenolates **37**(*Z*) and **37**(*E*). In contrast to the corresponding enolates **36b** derived from the $Cp_2Zr(C_2H_5)$ unit the $Cp_2Zr(Ph)$-containing products are formed as a kinetically controlled mixture at 80 ° C. It takes a temperature of 150 ° C to achieve a thermally induced *Z*/*E*-enolate equilibration. At equilibrium, again the *Z*-configurated metallocene enolate is the preferred isomer (**37**(*Z*)/**37**(*E*) = 84/16).

Conclusions

Chemical features of the group 4 metallocene ylides prepared via our novel route seem to be governed by two effects. First of all, the $Cp_2M(R)$-ylide substituents have to be regarded as very bulky groups. This steric effect clearly reduces the ability of the ylide moieties to function as nucleophilic reagents in Wittig type reactions. In the case where a substantial carbanionic character still seems to be present at the ylide carbon this can only manifest itself in the least sterically demanding reaction type, i.e. the abstraction of a proton from a suitably acidic substrate.

However, a strong electronic effect even reduces the basic properties of the metallocene ylides as compared to "ordinary" organic phosphorus ylides. There is considerable evidence for a significant ylide carbon-to-metal π-backbonding leading to a substantial reduction of the ylide character of the $MCH{=}PPh_3$ moiety. This effect strongly increases on going from hafnium to zirconium and titanium as the central metal. While the titanocene ylide does not even serve as a base against the ketones employed, the reduced basicity of the zirconocene ylides $Cp_2Zr(R)CH{=}PPh_3$ allows a remarkable control of the enolate forming reaction by the nature of the σ-hydrocarbonyl group bonded to zirconium [32 *].

Experimental

All manipulations of organometallic compounds and phosphorus ylides were carried out in an inert atmosphere (argon) employing Schlenk type glassware. Solvents were dried, distilled, and saturated with argon prior to use. The following spectrometers were used for characterizing novel compounds: NMR, Bruker WP80FT (^1H variable temperatur, 80 MHz; ^{31}P, 32 MHz), AM-200 FT (^1H, 200 MHz), WM-300 FT (^{13}C, 75.5 MHz), and WH 400 FT (^1H, 400 MHz); IR, Nicolet 7000 FT IR spectrometer; MS, Finnigan MAT CH7 and 311A spectrometers. Elemental analyses were carried out by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr. Melting points are uncorrected.

Preparations of organic ylides were carried out using standard procedures [33]. Pinacolone-d_3 was prepared by treatment of pinacolone with KOD/D_2O. The preparation and in depth characterization of the metallocene ylides mentioned in this paper have recently been described in several publications [6 *,12,17]. X-ray crystal structure analyses of the metallocene ylides $Cp_2Ti(Ph)CH{=}PPh_3$ (**26a**), $Cp_2Zr(Ph)CH{=}PPh_3$ (**26b**), and $Cp_2Hf(C_2H_5)CH{=}PPh_3$ (**21b**) have also recently been described by us [6 *]. Selected data originating from these studies have been included in Table 1.

Reaction of $Cp_2Zr(CH_2CH{=}CHCH_3)CH{=}PPh_3$ with benzophenone

A 240 mg (0.44 mmol) sample of the crotylzirconocene ylide (**16a**) (*cis/trans*-equilibrium mixture) was heated with 158 mg (0.87 mmol) benzophenone in 10 ml benzene-d_6 for 3 h at 50 °C. The reaction mixture was filtered and investigated by NMR spectroscopy. The ^1H NMR spectrum revealed that the starting material had been consumed completely to give 1,1-di-η-cyclopentadienyl-6,6-diphenyl-7-oxazirconacyclohept-3-ene (**28**) (identified by ^1H NMR comparison with authentic material [28] (200 MHz, benzene-d_6: δ 5.70 (s, 10H, Cp), 6.27 (q, 1H, H at C(3)), 5.00 (q, 1H, H at C(4)), 2.55 (d, 2H, H at C(5)), 1.83 (d, 2H, H at C(2)); coupling constants: ^3J(H(2),H(3)) 9 Hz, ^3J(H(3),H(4)) 10.4 Hz, ^3J (H(4),H(5)) 8.3 Hz), 1,1-diphenylethylene (independently prepared by Wittig-olefination of benzophenone with methylene triphenylphosphorane: ^1H NMR (benzene-d_6): δ 5.37 (s, CH_2)), and triphenylphosphine oxide (identified by ^{31}P NMR). These three products were formed in a 1/1/1 ratio.

Reaction of $Cp_2Zr(Ph)CH{=}PPh_3$ (26b) with pinacolone

NMR controlled experiment. A mixture of 65 mg (0.11 mmol) of ylide complex **26b** and 23 mg (0.23 mmol) pinacolone in 1 ml benzene-d_6 was heated to 80 °C. The yellow colour of the ylide disappeared after 3 h. (1-t-Butylethenolato)phenylzirconocene (**35b**) was identified as the only organometallic product formed. An equimolar amount of 2-t-butylpropene (identified by comparison with authentic material) was formed in addition to Ph_3PO.

Preparation of (1-t-butylethenolato)phenylzirconocene (35b)

Phenylzirconocene ylide (**26b**) (2.83 g, 4.94 mmol) and pinacolone (990 mg, 9.9 mmol) in 70 ml toluene were heated for 5 h at 80 °C. Solvent was then removed in vacuo and the residue extracted with 80 ml pentane. After filtration and removal of the pentane from the resulting solution 1.65 g (84%) **35b** was obtained as a colourless powder, m.p. 90 °C. Anal. Found C, 65.67, H 6.55. $C_{22}H_{26}OZr$ calcd.: (397.67) C 66.45, H 6.59%. ^1H NMR (benzene-d_6): δ 5.90 (s, 10H, Cp), 4.02, 3.73 (s, 1H each, $=CH_2$), 1.11 (s, 9H, CH_3), 7.10–7.60 (m, 5H, Ph) ppm. ^{13}C (benzene-d_6, ^1J(CH) in parentheses): δ 112.0 (172, Cp), 175.9 (O*C*(R)=), 84.6 (154, 159, $=CH_2$), 36.7 (*C*Me_3), 28.6 (126, CH_3), Ph: 179.0 (*ipso*), 138.1 (154, *ortho*), 127.5 (156, *meta*), 125.1 (*para*) ppm. IR (KBr): ν 1600 cm^{-1} (enolate C=C). MS, $m/e = 396$ (M^+), 319 ($M^+ -$ Ph), 220 (Cp_2Zr).

Reaction of $Cp_2Hf(C_2H_5)CH{=}PPh_3$ (21b) with pinacolone

NMR controlled experiment. A solution of 73 mg (0.12 mmol) ylide complex **21b** and 25 mg (0.24 mmol) pinacolone in 1 ml benzene-d_6 were kept at room temperature for 24 h. The ^1H NMR spectrum showed that only about 25% of the starting material had reacted. After additional 2 h at 80 °C the reaction was complete to give (1-t-butylethenolato)ethylhafnocene (**33b**) (see below for characterization), 2-t-butylpropene (identified by comparison with authentic material obtained via Wittig olefination from CH_3COCMe_3), and triphenylphosphine oxide (ratio 1/1/1).

Synthesis of (1-t-butylethenolato)ethylhafnocene (33b) on a preparative scale. A sample of 2.38 g (3.9 mmol) ethylhafnocene ylide (**21b**) is heated with 800 mg (0.8 mmol) pinacolone in 100 ml toluene for 5 h at 80 °C. Work-up as described in detail for the preparation of **35b** yielded **33b** as a yellow oil (1.48 g, 87%) that was characterized without further purification. ^1H NMR (benzene-d_6): δ 5.78 (s, 10H, Cp), 3.91, 3.55 (s, 1H each, $=CH_2$), 1.63 (t, ^3J 7 Hz, CH_3), 0.89 (q, CH_2), 1.05 (s, CMe_3) ppm. ^{13}C NMR (benzene-d_6, ^1J(CH) in parentheses): δ 110.1 (172, Cp), 175.3 (O*C*(R)=), 83.1 (154, 159, $=CH_2$), 36.9 (*C*Me_3), 28.5 (125, $C(CH_3)_3$), 36.3 (115, CH_2), 16.9 (124, CH_3) ppm.

Reactions of metallocene ylides with 1,1,1-trideutero-3,3-dimethylbutan-2-one (pinacolone-d_3)

$Cp_2Zr(Ph)CH{=}PPh_3$ (26b). A solution of 220 mg (0.38 mmol) metallocene ylide **26b** and 79 mg (0.76 mmol) pinacolone-d_3 in 4 ml of benzene-d_6 were heated for 5 h at 80 °C. Without further workup the resulting solution was investigated by ^1H NMR. Besides Ph_3PO we identified two products $Cp_2Zr(Ph)OC(CMe_3){=}CD_2$ **35b**-d_2 (^{13}C NMR: δ 112.1 (d, Cp), 175.8 (s, OC(R)=), 84.1 (quint. [1/2/3/2/1], ^1J(CD) 24.5 Hz, $=CD_2$), 28.6 (q, CH_3), 36.6 (s, *C*Me_3), Ph: 179.0 (s, *ipso*-C), 138.1 (d, *ortho*-C), 127.4 ppm (d, *meta*-C), 125.0 (d, *para*-C)) and $CD_3C(CMe_3){=}CHD$ (^{13}C NMR: δ 29.2 (q, CH_3), 35.8 (s, *C*Me_3), 153.7 (s, *C*=CHD), 107.9 ppm (t [1/1/1], ^1J(CD) 24 Hz, =*C*HD)).

*$Cp_2Hf(C_2H_5)CH{=}PPh_3$ (**21b**).* Metallocene ylide **21b** (240 mg, 0.39 mmol) and pinacolone-d_3 (81 mg, 0.79 mmol) in 4 ml of benzene-d_6 were heated for 10 h at 80 °C. The resulting solution was studied by NMR directly without workup. The only products found were Ph_3PO, $CD_3C(CMe_3){=}CHD$ and $Cp_2Hf(C_2H_5)OC(CMe_3){=}CD_2$ (**33b**-d_2) (^{13}C NMR: δ 110.1 (d, Cp), 175.3 (s, O*C*(R)=), 28.5 (q, C(*C*H_3)$_3$), 36.8 (s, *C*Me_3), 82.9 (quint. [1/2/3/2/1], ^1J(CD) 23.4 Hz, $=CD_2$), 36.3 (t, CH_2), 16.9 ppm (q, CH_3)).

Reaction of $Cp_2Zr(CH_2CH{=}CMe_2)CH{=}PPh_3$ with pinacolone

A toluene solution (30 ml) of 320 mg (0.57 mmol) dimethylallylzirconocene ylide (**31**) and 114 mg (0.11 mmol) pinacolone was heated for 3 h at 50 °C. Usual work-up (see above) yielded 210 mg (95%) of (1-t-butylethenolato)(σ-3,3-dimethylallyl)zirconocene (yellow oil). ^1H NMR (400 MHz, benzene-d_6): δ 5.85 (s, 10H, Cp), 3.97, 3.61 (s, 1H each, $=CH_2$), 1.07 (s, 9H, $C(CH_3)_3$), 1.94 (d, ^3J 8.8 Hz, 2H, CH_2), 5.78 (d, 1H, =CH), 1.97, 1.86 ppm (s, 3H each, CH_3). ^{13}C NMR (benzene-d_6, ^1J(CH) in parentheses): δ 111.3 (172, Cp), 176.0 (s, O*C*(R)=), 83.4 (154, 159, $=CH_2$), 36.8 (*C*Me_3), 28.5 (125, C(*C*H_3)$_3$), 43.9 (121, CH_2), 132.6 (146, CH_2*C*H=), 118.6 (=*C*Me_2), 18.2 (125, *Z*-CH_3), 26.1 ppm (125, *E*-CH_3).

*Reaction of $Cp_2Zr(Ph)CH{=}PPh_3$ (**26b**) with propiophenone*

NMR controlled experiment. Metallocene ylide **26b** (69 mg, 0.12 mmol) and propiophenone (32 mg, 0.24 mmol) dissolved in 1 ml benzene-d_6 were treated at 80 °C for 4 h. *E*- and *Z*-(1-phenylpropenolato)phenylzirconocene (**37**) (*Z*/*E* = 55/45, identification see below), 2-phenyl-1-butene (independently prepared by Wittig olefination of propiophenone with methylene triphenylphosphorane for identification), and Ph_3PO were the only products found in the reaction mixture.

Preparative scale. A solution of 2.3 g (4 mmol) of **26b** and 1.08 g (8 mmol) of propiophenone in 100 ml benzene was heated for 5 h at 80 °C. Solvent was then removed in vacuo, the residue extracted with 100 ml of pentane. The mixture was stirred for 30 min and filtered from the precipitated triphenylphosphine oxide. Solvent was removed in vacuum. The oily residue was "dried" in vacuo for 3 h at 60 °C to remove residual traces of the ketone starting material. The mixture of Zr-enolate isomers was obtained as a colourless oil (1.48 g, 86%). ^1H NMR (CD_2Cl_2, *Z*/*E* ratio 55/45, *E*-isomer in brackets): δ 6.16 [6.11] (s, 10H, Cp), 4.87 [4.80] (q, 3H, 7 Hz, 1H, =CH), 1.71 [1.65] (d, CH_3), 7.00–7.60 ppm (m, Ph). ^{13}C NMR (CD_2Cl_2, ^1J(CH) in parentheses, chemical shifts of the *E*-isomer in brackets): δ 112.9 [112.3] (173, Cp), 160.3 [160.3] (O*C*(Ph)=), 98.4 [99.9] (153, =*C*HCH_3), 12.2 [13.2] (126, =CH*C*H_3) ppm; enolate Ph: δ 140.8 [138.9] (*ipso*-C), 126.2 [128.6] (*ortho*-C), 128.3 [128.3] (*meta*-C), 127.5 [127.8] (*para*-C); Zr–Ph: 178.6 [179.3] (*ipso*-C), 139.0 [138.5] (156, *ortho*-C), 127.0 [127.1] (158, *meta*-C), 124.9 [124.7] (158, *para*-C) ppm.

Thermally induced *Z*/*E*-isomerization. A sample of a CD_2Cl_2 solution containing the isomeric enolate complexes **37**(*Z*) and **37**(*E*) was sealed in a 5 mm NMR tube and heated to 150 °C in an autoclave for several hours. The changing *Z*/*E*-enolato ratio was followed by ^1H NMR at ambient temperature: (t(h), **37**(*E*)/**37**(*Z*) ratio: 0, 45/55; 2, 30/70; 9. 16/84; 25, 16/84).

Reaction of $Cp_2Hf(C_2H_5)CH{=}PPh_3$ *(**21b**) with propiophenone*

Treatment of propiophenone (240 mg, 1.8 mmol) with ethylhafnocene ylide **21b** (550 mg, 0.9 mmol) as described above for the reaction of the aromatic ketone with **26b** yielded 400 mg (95%) of a *E*/*Z*-ethylhafnocene enolate (**36b**) mixture (colourless viscous oil). ^{1}H NMR (toluene-d_8, *Z*/*E*-ratio 87/13; *E*-isomer in brackets): δ 5.71 [5.72] (s, 10H, Cp), 4.87 [4.66] (q, ^3J 7 Hz, 1H, $=CHCH_3$), 1.69 [1.75] (d, 3H, $=CHCH_3$), 0.97 [0.86] (q, ^3J 7.7 Hz, 2H, $HfCH_2$), 1.61 [1.60] (t, 3H, CH_2CH_3), Ph: 7.39 [7.34] (d, *ortho*-H), 7.00–7.20 ppm (m, *meta*-H, *para*-H, both isomers). ^{13}C NMR (CD_2Cl_2, ^1J(CH) in parentheses, *E*-isomer chemical shifts in brackets): δ 111.0 [110.5] (173, Cp), 37.0 [36.0] (116, $HfCH_2$), 16.8 [16.7] (123, CH_2CH_3), 159.3 [159.3] (OC(Ph)=), 97.6 [99.5] (155, $=CHCH_3$), 11.7 [13.2] (126, $=CHCH_3$), Ph: 140.7 [139.1] (*ipso*-C), 125.4 (159, *ortho*-C), 128.3 (160, *meta*-C), 127.3 [127.5] (160, *para*-C) ppm.

Thermolysis: A sealed ^{1}H NMR sample of the 87/13 *Z*/*E*-hafnocene enolate mixture in CD_2Cl_2 was thermolyzed for 2 h each at 130, 150 and 180 °C. The **36b**(*Z*/*E*) ratio was determined by integration of the corresponding ^{1}H NMR Cp signals. The *Z*/*E*-ratio remained unchanged. Heating at 180 °C caused some decomposition.

Reaction of $Cp_2Zr(C_2H_5)CH{=}PPh_3$ *(**21a**) with propiophenone*

A sample of 220 mg (0.42 mmol) ethylzirconocene ylide **21a** and 112 mg (0.84 mmol) propiophenone was treated at 80 °C in benzene solution as described for **26b** (see above). A mixture of *E*/*Z*-isomers of (1-phenyl-1-propenolato)ethylzirconocene (**36a**) was obtained (150 mg, 93%, colourless oil). ^{1}H NMR (toluene-d_8, $\geqslant$ 95% *Z*-isomer): δ 5.75 (s, 10H, Cp), 1.14 (q, ^3J 7.8 Hz, 2H, $ZrCH_2$), 1.49 (t, 3H, CH_2CH_3), 4.93 (q, ^3J 6 Hz, 1H, $=CHCH_3$), 1.66 (d, 3H, $=CHCH_3$), 7.1–7.4 (arom. H) ppm. ^{13}C NMR (CD_2Cl_2, *Z*/*E*-ratio 95/5, ^1J(CH) in parentheses, *E*-isomer chemical shifts in brackets: δ 111.8 [111.3] (172, Cp), 36.9 [35.4] (117, $ZrCH_2$), 17.3 [17.1] (124, CH_2CH_3), 159.5 [159.8] (OC(Ph)=), 97.0 [99.2] (155, $=CHCH_3$), 11.7 [13.2] (126, $=CHCH_3$), Ph: 140.6 [139.1] (*ipso*-C), 125.3 (159, *ortho*-C), 128.3 (160, *meta*-C), 127.2 (160, *para*-C) ppm.

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