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THERMALLY INDUCED REACTION OF THE YLIDE $CH_3CH{=}PPh_3$ WITH DIARYLZIRCONOCENE COMPLEXES; THE FORMATION OF UNUSUAL METALLACYCLIC PHOSPHA-ALLYL TYPE PRODUCTS *

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Summary

Diphenylmetallocene complexes $(RCp)_2ZrPh_2$ (**4a**, **4b**: $R = H, CH_3$) react with the phosphorous ylide $Ph_3P{=}CHCH_3$ (**5**) at 80 °C to yield six-membered metallacyclic ylides $(RCp)_2\overline{ZrCH_2CH{=}P(Ph)_2(C_6}H_4)$ (**8a,8b**) plus two equivalents of benzene. The reaction presumably proceeds through a thermally generated (η^2-benzyne)zirconocene intermediate which takes up **5** to form a metallocene ylide $(RCp)_2Zr(Ph)C(CH_3){=}PPh_3$ (**6**). β-Hydride elimination and readdition followed by *ortho*-metallation then leads to the six-membered metallacycle. Complexes **8** have a stable chiral ground state geometry as judged by NMR spectroscopy. The presence of a distorted Cp_2Zr (phospha-allyl) moiety is suggested to explain the observed characteristic spectroscopic features of the metallacyclic ylides **8**.

Transition metal complexes can react with ylides in several ways [1]. Simple 1/1 adducts (ylide complexes) can be formed. These often exhibit phosphonium salt behavior and undergo proton transfer reactions [2]. We have recently used this ability of the $L_nMCH_2PPh_3$ moiety to carry out a novel synthesis of group 4 metallocene ylides [3]. Reactive intermediates of the (η^2-olefin)-MCp_2-type were generated in the presence of $CH_2{=}PPh_3$. Trapping of the organometallic d^2-configurated 16-electron intermediates followed by intramolecular proton transfer yielded metallocene ylides $Cp_2M(R)CH{=}PPh_3$. These are very interesting substrates, that exhibit substantial M–C (ylide) double bond character which increases in strength on going from hafnium to zirconium and titanium as the central metal atom. In two special cases the starting materials being (η^2-ethylene)HfCp [4] or (η^2-aryne)-

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* Dedicated to Professor Jean Tirouflet on the occasion of his retirement.

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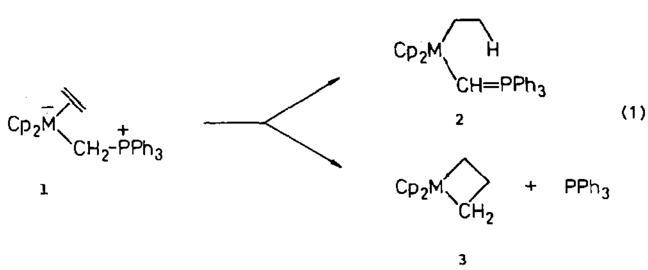
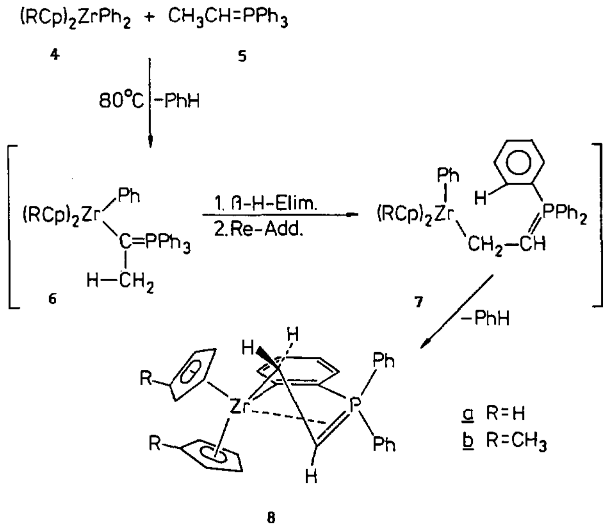


$TiCp_2$ [5]), the intramolecular H-migration is accompanied by a competing methylene transfer to form four-membered metallacycles and free triphenylphosphane (eq. 1). However, this characteristic behavior was only observed when the simple unsubstituted ylide methylene triphenylphosphorane was employed as a trapping agent for thermally generated reactive (olefin)metallocene complexes. We have treated (η^2-alkene)- [4], (η^2-aryne)- [6], and (η^2-conjugated diene)MCp_2 complexes [7] (M = Ti, Zr, Hf) with a variety of substituted ylides $RCH{=}PPh_3$ (R = CH_3, vinyl, phenyl, n-alkyl) but only for one of these combinations did we observe a reaction leading to well defined products. At elevated temperatures $CH_3CH{=}PPh_3$ cleanly readts with diarylzirconocene complexes. However, this reaction takes a somewhat different course from the ones employing the parent ylide $CH_2{=}PPh_3$ (see eq. 2).

Results and discussion

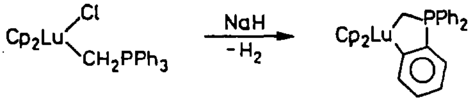
The ylide $CH_3CH{=}PPh_3$ (**5**) reacts cleanly with diphenylzirconocene (**4a**) at 80 ° C. A single product **8a** was isolated in ca 80% yield after crystallization from toluene/hexane (1/1). Unfortunately, the large red crystals of **8a** thus obtained were not suitable for a structure determination by X-ray diffraction, but fairly detailed structural information was obtained from other analytical data. From its elemental analysis and mass spectrum ($m/e = 508$, M^+), compound **8a** appears to be formally a 1/1 adduct of the fragments $C_{20}H_{17}P$ and zirconocene $(C_5H_5)_2Zr$. This characteristic composition of the reaction product was confirmed by the result of the thermolysis (80 ° C) of di(*p*-tolyl)zirconocene (**4c**) in the presence of ethylidene triphenylphosphorane (**5**), again **8a** was the only observed product. When the starting material is $Cp_2Zr(p\text{-tolyl})_2$, two equivalents of toluene have to be liberated on forming **8a**, and this was shown to be the case by ^1H NMR monitoring of the reaction between **4c** and **5** in benzene-d_6 solution at 80 ° C.

The new compound **8** may be formed via a pathway through intermediates **6** and **7** (see Scheme 1). We assume that the metallocene ylide **6** is formed in the usual way by addition of the ylide to very reactive thermally generated (η^2-aryne)zirconocene followed by an intramolecular hydrogen migration [3]. This leads to the regeneration of a zirconium bound aryl group. In contrast to the stable (phenylzirconocenyl)ylide $Cp_2Zr(Ph)CH{=}PPh_3$ (prepared by the analogous reaction between thermally generated (η^2-benzyne)$ZrCp_2$ and methylene triphenylphosphorane) [3] $Cp_2Zr(Ph)C(CH_3){=}PPh_3$ has β-hydrogens in the ylide substituent. The primary reaction product **6** is therefore susceptible to a β-hydride elimination/readdition reaction sequence that leads to the rearranged product **7**. This in turn could react further by cleavage of an *ortho*-C–H bond of a P-bound phenyl group to give a second equivalent of the arene and form the metallacyclic *ortho*-metallation product **8**.



SCHEME 1

Similar examples of ring-forming *ortho*-metallation reactions have been observed in reactions starting from Cp_2Lu-(alkyl) or -(hydride)$CH_2{=}PPh_3$ complexes [8].



(2)

The NMR spectra of **8a** are typical for a compound having ylide character ($ArPh_2P{=}CH$: δ 27.8 (^{31}P), 0.84 (^{1}H), 14.2 ppm (^{13}C NMR). However, unusually, the ^{13}C NMR spectrum of **8a** clearly exhibits signals of two chemically different phenyl groups at phosphorus. The third aryl substituent is connected to the metal via the *ortho*-position; the *ipso*-carbon atoms of this phenylene moiety exhibit very characteristic ^{13}C chemical shifts (δ 199.5 (Zr–C); 152.3 (P–C) ppm).

The zirconium-bound Cp ligands give rise to two resonances in both the ^{1}H and in the ^{13}C NMR spectra. Consequently, the hydrogen atoms of the CH_2 group connecting the metal center and the ylide carbon atom are also diastereotopic giving signals at δ 1.95 and 0.83 ppm in the ^{1}H NMR spectrum (^{2}J(H,H) 10.3 Hz). Two rather different ^{1}J(C,H) coupling constants of 140 and 146 ppm complete the characteristic features of this CH_2 group within the metallacyclic framework of **8a**.

Complex **8b**, which was produced analogously from bis(η-methylcyclopentadienyl)zirconium diphenyl (**4b**) and $Ph_3P{=}CHCH_3$ (**5**) exhibits the same spectroscopic characteristics. Owing to the diastereotopism of the Cp ligands, two methyl group singlets and eight signals for the MeCp-methine CH groups are observed for **8b**.

From these observations it is evident that **8** has a six-membered metallacyclic structure in a chiral conformation. The ^{1}H NMR NOE difference spectra of **8a** revealed the positions of the CH_2- and ylide CH-hydrogens relative to each other and to the Cp-hydrogens. These measurements indicate that the hydrogens of the CH_2 group lie in the vicinity of one of the Cp ligands, whereas the ylide CH-proton adjoins the other zirconium-bound η-cyclopentadienyl moiety. Thus, **8** seems to adopt a conformation of the half-chair type (see Scheme 1).

However, the inversion activation barrier for such a situation is usually very low if the chiral ground state structure arises from purely steric interactions; e.g. the interconversion of cyclohexene (chiral) half chairs through the achiral half boat conformation has an activation barrier of only 6 kcal/mol [9]. Furthermore Schmidbaur's work on six-membered "endocyclic" ylides has given no indication of an unusually high stabilization of their chiral ground state conformations [10].

For **8** the topomerization process should result in an equilibration of the pairs of diastereotopic Cp ligands on zirconium and the hydrogen atoms of the α-CH_2 group or in the phenyl ligands on phosphorus. We have in spite of a careful search been unable to find any evidence for such a ring-inversion in the case of **8**.

Since there was no indication of exchange of diastereotopic groups which would become detectable by ordinary dynamic NMR spectroscopy, we performed ^1H NMR magnetization transfer experiments on **8b** but no dynamic effect was observed to the maximum temperature used (T 353 K).

It is not obvious why the chiral geometry of the metallacyclic ring structure of system **8** should be so stable. It cannot be ruled out that the incorporation of the two heteroatom-centered systems Cp_2Zr and $P(Ph)_2{=}CH$ together with the 1,2-phenylene moiety introduces an extra rigidity to the framework of the six-membered ring system. However, it is more likely that the observed favoured geometry of the system may be due to interaction of the ylide P=C moiety with the coordinatively unsaturated transition metal center across the ring. One possibility is a metal-phospha-π-allyl type interaction, which would represent an electronically stabilized chiral situation. Several examples of very stable non-cyclic (phospha-) and (diphospha-π-allyl) metal complexees have been described recently [11]. The relatively large $^1J(C(1),H)$ coupling constants of the methylene carbon (140, 146 Hz) could be interpreted as indicating that this carbon atom has a hybridization approaching sp^2, even though the geminal coupling constant $|^2J(H(1),H(1'))|$ of 10.3 Hz would be very large for an η^3-allyl system.

To obtain additional information, we measured the $^{13}C,^{13}C$-coupling constant of the Zr-CH_2-$CH{=}P$ linkage in **8b** [12]. For an η^3-allyl system a coupling constant of 40–45 Hz would be expected [13]. The measured value of $^1J(C(1),C(2))$ is only 31.2 Hz, significantly smaller than even the coupling between two sp^3 carbon atoms in ethane (34.6 Hz). Since C(2) has a hybridization between sp^2 and sp^3, there must be considerably less than the 25% s-character from C(1) in the C(1)–C(2) bond [14]. This observation is typical of strained hydrocarbons and suggests that the Zr–C–C angle in the complexes **8** is less than tetrahedral. This is also consistent with the magnitude of the coupling constants $^1J(C(1),H)$, and the observed geminal coupling between the protons at C(1) [15].

We therefore conclude that the metal atom is essentially σ-bonded to the CH_2 group but that an additional interaction with the ylide moiety (as depicted in Scheme 1) is present to stabilize the preferred chiral "conformation" of these metallacyclic compounds. The Zr–C(1)–C(2) bond angle must therefore the relatively small.

Experimental

All manipulations of organometallic compounds and ylides were carried out under argon by use of standard Schlenk type glassware. Solvents were dried, distilled, and saturated with argon prior to use. Spectra were obtained with Bruker WP80 FT (^{1}H variable temperature, 80 MHz; ^{31}P, 32 MHz), WM300 FT (^{13}C, 75.5 MHz), and WH400 FT (^{1}H, 400 MHz) NMR spectrometers, a Nicolet 7000FT IR spectrometer, and a Finnigan MAT CH 7 311 mass spectrometer. Elemental analyses were carried out by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr. Melting points are uncorrected. Diarylmetallocene complexes and the organic ylide were prepared by standard procedures.

Reaction of diphenylzirconocene with ethylidene triphenylphosphorane

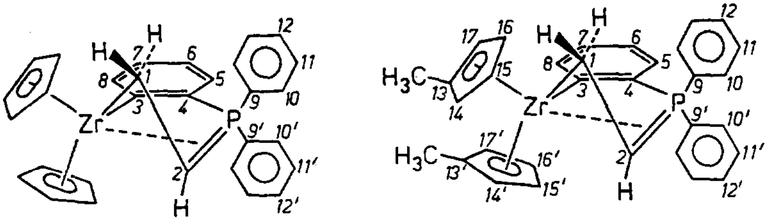
A solution of diphenylzirconocene (**4a**) (2.75 g, 7.36 mmol) and ethylidene triphenylphosphorane (**5**) (2.56 g 8.8 mmol) in 75 ml of heptane is heated for 5 h at 80 ° C, during which a light brown solid begins to precipitate from the hot solution. The mixture is allowed to cool to room temperature and the solution decanted from the precipitate. The solid residue is suspended in 50 ml pentane, then filtered off, and dried in vacuo to yield 2.95 g (78.5%) of **8a**. The complex is recrystallized from hot toluene/hexane (1/1) to give large red crystals, m.p. 145 ° C. Anal. Found: C, 71.06; H, 5.13. $C_{30}H_{27}PZr$ (509.73) calcd.: C, 70.69; H, 5.34%. ^{1}H NMR (400 MHz; ppm, C_6D_6); δ 5.49, 5.00 (s, 5H each, Cp), 1.95 (m, 1H, H(1′); ^{2}J(H(1),H(1′)) −10.3 Hz, ^{3}J(H(1′),H(2)) 8.5 Hz, ^{3}J(H,P) 16.4 Hz), 0.83 (m, 1H, H(1); ^{3}J(H(1),H(2)) 13.1 Hz, ^{3}J(H,P) 1.1 Hz), 0.84 (m, 1H, H(2); ^{2}J(H,P) 21.2 Hz), 8.16 (m, 1H, H(8); ^{4}J(H,P) 1.8 Hz), 7.22 (m, 1H, H(7); ^{5}J(H,P) 2.4 Hz, ^{3}J(H(7),H(8)) 7.3 Hz, ^{3}J(H(7),H(6)) 7.1 Hz, ^{4}J(H(7),H(5)) 1.4 Hz), 7.46, 7.28 (m, 1H each, H(10), H(10′)), 6.88 (m, H(11), H(11′)), 7.75, 6.99 (m, remaining Aryl-H). ^{31}P NMR (C_6D_6): δ 27.8 ppm. ^{13}C NMR (C_6D_6) (ppm): δ 103.5, 103.6 (d, ^{1}J(C,H) 170 Hz, Cp), 14.2 (dd, ^{1}J(C,H) 142 Hz, ^{1}J(C,P) 89.8 Hz, C(2)), 31.4 (dt, ^{1}J(C,H) 140, 146 Hz, ^{2}J(C,P) 11.4 Hz, C(1)), 199.5 (d, ^{2}J(C,P) 47.8 Hz, C(3)), 152.3 (d, ^{1}J(C,P) 128 Hz, C(4)), 143.2 (dd, ^{1}J(C,H) 156 Hz, ^{3}J(C,P) 21.8 Hz, C(8)), 123.2 (dd, ^{1}J(C,H) 160 Hz, ^{2}J(C,P) 13.1 Hz, C(5)), 127.6 (dd, ^{1}J(C,H) 156 Hz, ^{4}J(C,P) 3.7 Hz, C(7)), 131.3 (dd, ^{1}J(C,H) 160 Hz, ^{3}J(C,P) 22.4 Hz, C(6)), 125.7, 137.1 (d, ^{1}J(C,P) 81.8, 55.9 Hz, C(9),C(9′)), 134.2, 130.8 (dd, ^{1}J(C,H) 162 Hz, ^{2}J(C,P) 8.1, 9.1 Hz, C(1), C(10′)), 129 (dd, ^{3}J(C,P) 10 Hz, C(11), C(11′), 132.1, 130.5 (dd, ^{1}J(C,H) 160 Hz, ^{4}J(C,P) 2 Hz, C(12), C(12′). IR (KBr): ν 3100, 1430, 1020, 790 (Cp) cm^{-1}. MS (508) (M^+), 220 (Cp_2Zr).

Reaction of bis(p-tolyl)zirconocene (4c) with ethylidene triphenylphosphorane

A solution of equimolar amounts of the starting materials **4c** and **5** (ca. 60 mg each) in 0.6 ml benzene-d_6 is sealed in a 5 mm diameter NMR tube. then kept at 80 ° C for 5 h. After that time the ^{1}H NMR spectrum shows that an almost quantitative amount of **8a** has been formed along with two molar equivalents of toluene (determined by integration of the CH_3 signals and Cp resonances relative to a silicone standard).

Reaction of bis(η-methylcyclopentadienyl)diphenylzirconium (4b) with ethylidene triphenylphosphorane

A solution of 3.95 g (9.8 mmol) of the diphenylmetallocene complex **4b** and 3.03 g (10.4 mmol) ethylidene triphenylphosphorane in 100 ml heptane is kept at 80 ° C for 6 h. The red precipitate which appears on cooling to room temperature, is filtered off (yield: 3.02 g, 57.5%), then recrystallized from boiling heptane to give large red crystals, m.p. 175 ° C. Anal. Found: C, 71.06; H, 5.92. $C_{32}H_{31}PZr$ (537.79)



SCHEME 2

calcd.: C, 71.47; H, 5.81%. ^{1}H NMR (400 MHz; ppm, C_7D_8): δ 1.73 (m, 1H, H(1′); ^2J(H(1),H(1′)) −8.1 Hz, ^3J(H(1′),H(2)) 9.8 Hz, ^3J(H,P) 16.0 Hz), 0.67 (m, 1H, H(1); ^3J(H(1),H(2)) 13.0 Hz, ^3J(H,P) 1.7 Hz), 0.55 (m, 1H, H(2); ^2J(H,P) 20.9 Hz, 1.85, 1.99 (s, 3H each, CH_3), 3.97, 5.20 (m, 1 H each, H(14), H(14′)), 5.05, 5.20 (m, 1H each, H(17), H(17′)), 4.90 5.48 (m, 1H each, H(15), H(15′)), 4.72, 5.46 (m, 1H, H(16), H(16′)), 8.14 (m, 1H, H(8); ^3J(H(8),H(7)) 7.4 Hz, ^4J(H,P) 2 Hz), 7.20 (m, 1H, H(7)); ^3J(H(7),H(6)) 7 Hz, ^5J(H,P) 2.4 Hz), 6.91 (m, 1H, H(6); ^3J(H(6),H(5)) 7.8 Hz, ^4J(H,P) 5 Hz), 7.52, 7.31 (m, 1H each, H(10), H(10′); ^3J(H,P) 11 Hz), 7.00 (m, remaining Aryl-H). ^{31}P NMR (C_7D_8): δ 27.8 ppm. ^{13}C NMR (C_6D_6) (ppm): δ 15.4, 15.5 (q, ^1J(C,H) 126 Hz, CH_3), 113.7, 114.8 (s, C(13), C(13′)), 98.2, 100.1, 102.9, 104.3, 106.6, 107.0, 107.3, 108.2 (d, ^1J(C,H) 167–170 Hz, C(14)–C(17), 17.7 (dd, ^1J(C,H) 143 Hz, ^1J(C,P) 89.6 Hz, C(2)), 36.1 (dt, ^1J(C,H) 140, 144 hz, ^2J(C,P) 11.6 Hz, ^1J(C(1),C(2)) 31.2 Hz, C(1)), 201.4 (d, ^2J(C,P) 47.9 Hz, C(3)), 152.2 (d, ^1J(C,P) 128 Hz, C(4)), 142.7 (dd, ^1J(C,H) 155 Hz, ^3J(C,P) 22.3 Hz, C(8)), 127.7 (dd, ^1J(C,H) 153 Hz, ^4J(C,P) 3.4 Hz, C(7)), 131.3 (dd, ^1J(C,H) 157 Hz, ^3J(C,P) 22.4 Hz, C(6)), 123.2 (dd, ^1J(C,H) 158 Hz, ^2J(C,P) 13.2 Hz, C(5)), 125.8, 137.3 (d, ^1J(C,P) 81.4, 55.1 Hz, C(9), C(9′)), 130.7, 134.2 (dd, ^1J(C,H) 160, 162 Hz, ^2J(C,P) 8.7, 8.1 Hz, C(10), C(10′)), 128.9, 129 (dd, ^3J(C,P) 10 Hz, C(11), C(11′)), 130.4, 132.2 (dd, ^1J(C,H) 160, 162 Hz, ^4J(C,P) 2.8, 2.6 hz, C(12), C(12′)). MS (536): $m/e = 536$ (M^+), 248 $(MeCp)_2Zr$).

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