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Bis(η^5-cyclopentadienyl)- and bis(η^5-indenyl)metallacycles of titanium and zirconium from methylenecyclopropanes by oxidative coupling

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Dedicated to Professor François Mathey on occasion of his 60th birthday

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Abstract

Methylenecyclopropane (**1a**) reacts with bis(trimethylphosphane)titanocene (**8**) and (η^2-1-butene)(trimethylphosphane)zirconocene (**12a**) via olefin complexes; e.g. **9**, in a [2+2] cycloaddition to afford the metallacyclopentane derivates **10**, **13** and **14**. In contrast, a [3+2] cycloaddition reaction is observed with bis(η^5-lndenyl)(η^2-1-butene)(trimethylphosphane)zirconium (**12b**) to furnish the 1-zircona-4-methylenecyclohexane **15**. Similarly, reactions of the complexes **8** and **12a** with benzylidenecyclopropane (**1c**) give the olefin complexes **9c** and **20**, while a direct reaction between the indenyl complex **12b** with **1c** occurs to furnish the 1-zircona-2-benzylidenecyclobutane complex **21b** which was characterised by X-ray crystallography. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Methylenecyclopropane; Titanocene(II) and zirconocene(II) complexes; Bis(η^5-indenyl)zirconium complexes; [2+2] and [3+2] Cycloadditions

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1. Introduction

Some time ago, we developed a method with which methylenecyclopentane derivatives can be prepared directly from methylenecyclopropanes (**1**) and alkenes via a transition metal-catalysed [3+2] cycloaddition [1]. Suitable catalysts for this process are, above all, nickel(0) and palladium(0) complexes. Since methylenecyclopropane itself [2] as well as its derivatives substituted on the ring [3] or the double bond [4] are readily accessible on a multi-gram scale and because numerous, variously substituted alkenes can be employed, this method is excellently suitable for the synthesis of very differently substituted mono- and bicyclic methylenecyclopentanes. In addition, these cycloadditions can proceed by different reaction pathways depending on the catalyst used. Consequently, the targeted (regioselective) synthesis of methylenecyclopentanes with differing substitution patterns is possible (Scheme 1).

Even now, the exact mechanisms of the two reaction routes are not completely understood. However, from the products obtained it is apparent that with a Pd(0) catalyst the distal bond and with a Ni(0) catalyst the proximal bond of the three-membered ring is cleaved. Two possibilities have been discussed for the proximal bond cleavage. Noyori et al. proposed a direct attack of the nickel catalyst at this bond with a 2-methylene-1-nickelacyclobutane complex **3a** as an intermediate of the catalysis [5]. The observation in cyclodimerisations and cyclotrimerisations of methylenecyclopropanes that cyclobutane and cyclopentane derivatives are formed led to the suggestion that both products are formed from a common intermediate. Accordingly, the primary product is the metallacyclopentane derivative **4a** or **4b** that can rearrange to the metallacyclohexane derivative **5a** or **5b**. The reaction products then arise via reductive eliminations from **4a**, **4b** and **5a**, **5b** (Scheme 2) [6,7].

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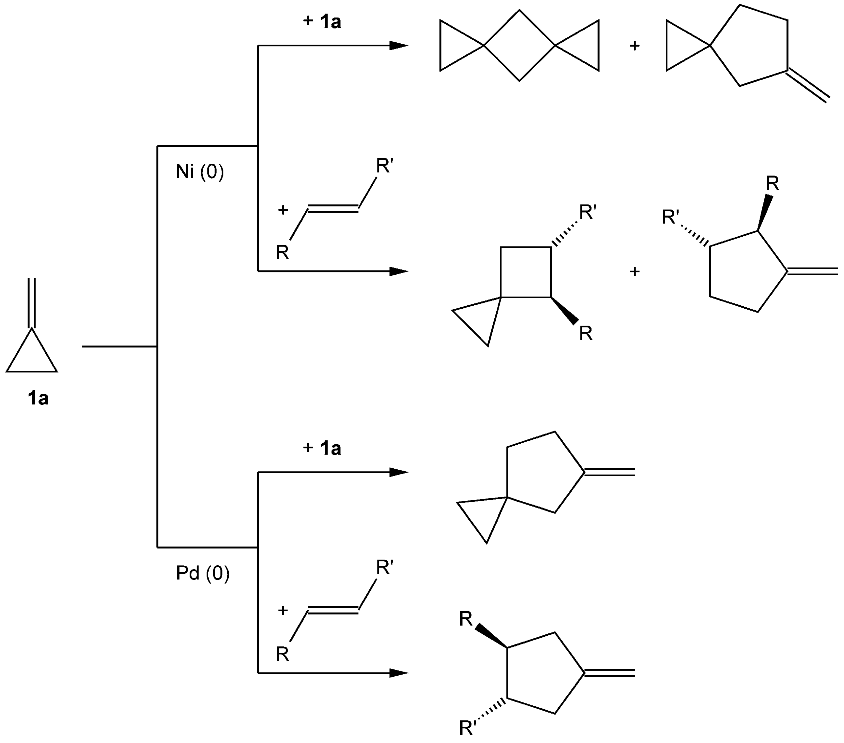
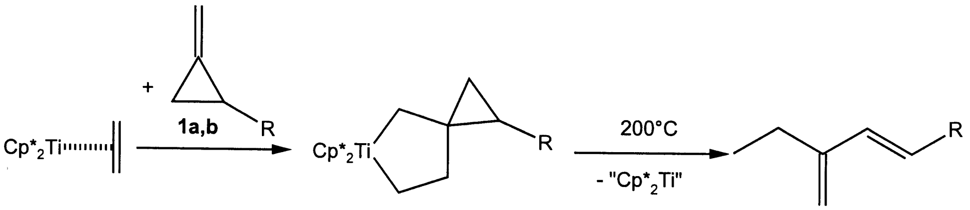


Scheme 1. Ni(0)- and Pd(0)-catalysed [2+2] and [3+2] cycloadditions with methylenecyclopropane (**1a**).

This proposal is supported by the isolation and characterisation of model compounds such as **2a** and **4a** [$L_2 = \alpha,\alpha'$-bipyridyl, 1,2-bis(dicyclohexylphosphanyl)-ethane, 1,2-bis(dimethylphosphanyl)ethane] from which the observed products can be obtained in a second reaction step [8].

It is known that metallocene derivatives of titanium(II) and zirconium(II) readily participate in oxidative coupling reactions with alkenes and alkynes to afford metallacyclopentane, metallacyclopentene and metallacyclopentadiene derivatives [9]. Thus, it seemed reasonable to examine the behaviour of methylenecyclopropanes with this class of compounds in more detail. Previous work had shown that methylenecyclopropane (**1a**) and 2-phenylmethylenecyclopropane (**1b**) reacted with bis(η^5-pentamethylcyclopentadienyl)(ethene)titanium to afford the corresponding titanacyclopentane derivatives **6a**,**b** which, upon heating to 200 °C, underwent preferential rearrangement to the 1,3-dienes **7a** and **7b** (Eq. 1) [10].

We now report on the reactivity of **1a** and benzylidenecyclopropane (**1c**) towards readily accessible metallocene(II) complexes such as $Cp_2Ti(PMe_3)_2$ [11], $Cp_2Zr(PMe_3)(\eta^2$-butene) [11] and analogous bis(η^5-indenyl)zirconium complexes [12]. We found that **1** can react with the tested metallocene derivatives to furnish η^2-olefin complexes, metallacyclopentane derivatives and, via proximal cleavage of the three-membered ring, metallacyclobutane derivatives. By combination of π-complex formation and ring opening processes a direct route to metallacyclohexane derivatives became available.



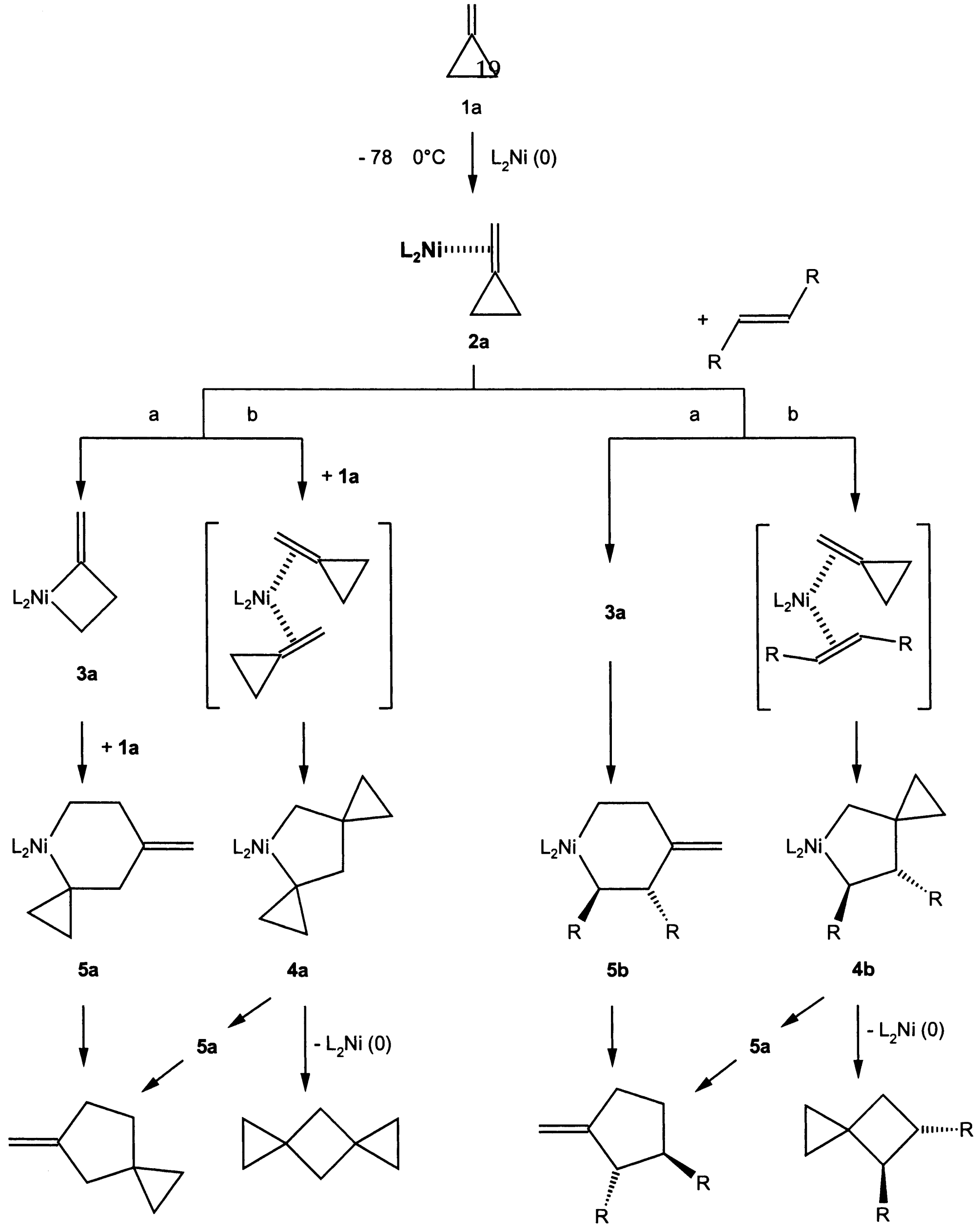
(1)

6a,b

7a,b

1a, **6a**, **7a**: R = H

1b, **7b**, **8b**: R = Ph

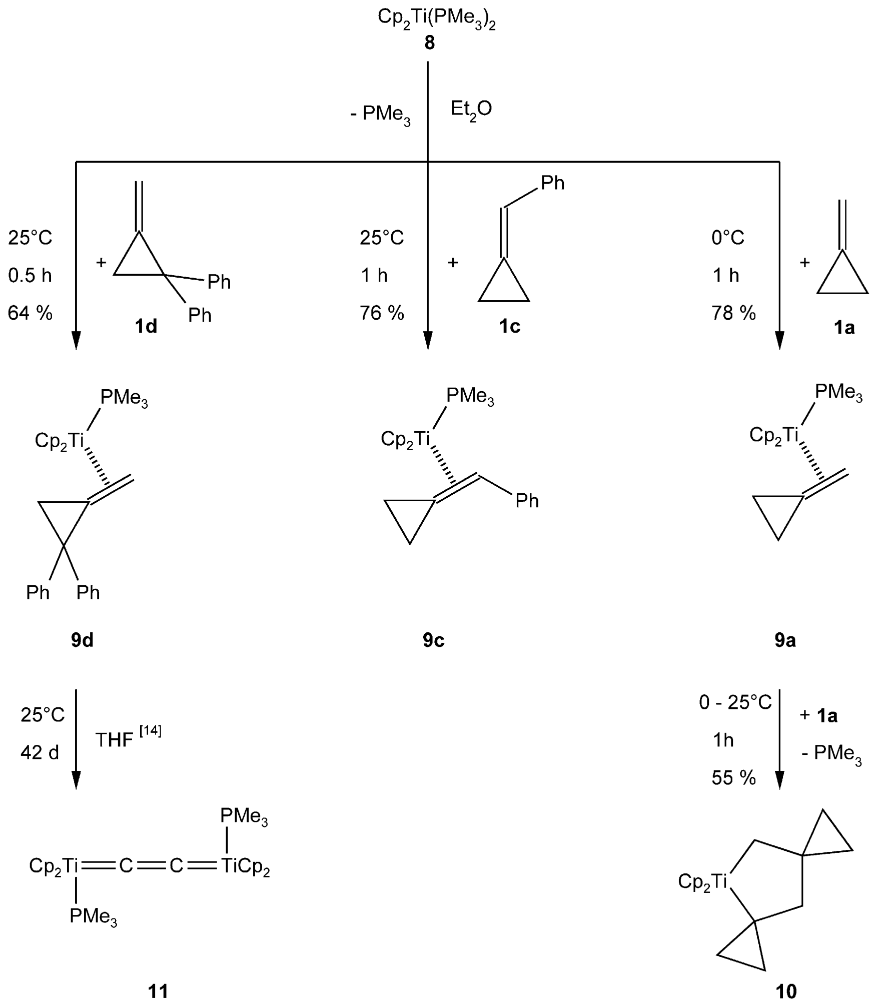


Scheme 2. Ni(0)-catalysed [2+2] and [3+2] cycloadditions with methylenecyclopropane (**1a**): possible reaction paths.

2. Results and discussion

Bis(η^5-cyclopentadienyl)bis(trimethylphosphane)titanium(II) (**8**) [11,13] and bis(η^5-cyclopentadienyl)-trimethylphosphane(η^2-1-butene)zirconium (**12**) [11,13] proved to be the most suitable starting materials for the preparation of olefin complexes and coupling products of methylenecyclopropanes with metallocenes of titanium and zirconium. The reaction of **8** with an equimolar amount of **1a** at 0 °C affords the olefin complex **9a** as a red powder in 78% yield. Use of excess **1a** under otherwise identical reaction conditions leads regioselectively to the titanacyclopentane derivative **10**. In contrast, reactions of **8** with the substituted methylenecyclopropanes **1c** and **1d** stop at the stage of the olefin complexes **9c** and **9d** [14]. The latter are obtained as red powders in yields of 76 and 64%, respectively. Upon longer standing in solution product **9d** undergoes rearrangement to the biscarbene complex **11** [14] (Scheme 3).

A decisive influence of the structures of the two cyclopentadienyl units on the course of the reactions with the methylenecyclopropanes **1a** and **1c** is observed when the bis(η^5-cyclopentadienyl)(butene)zirconium complex **12a** and the respective bis(η^5-indenyl)zirconium complex **12b** are used as starting materials. In

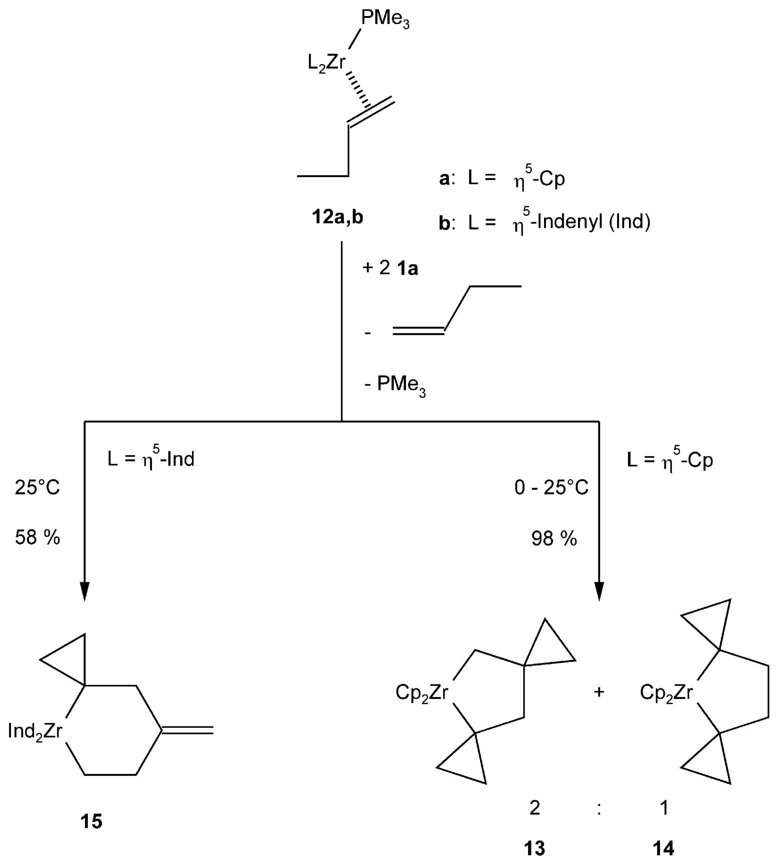


Scheme 3. Reactions of $Cp_2Ti(PMe_3)_2$ (**8**) methylenecyclopropane **1a**, **1c** and **1d**.

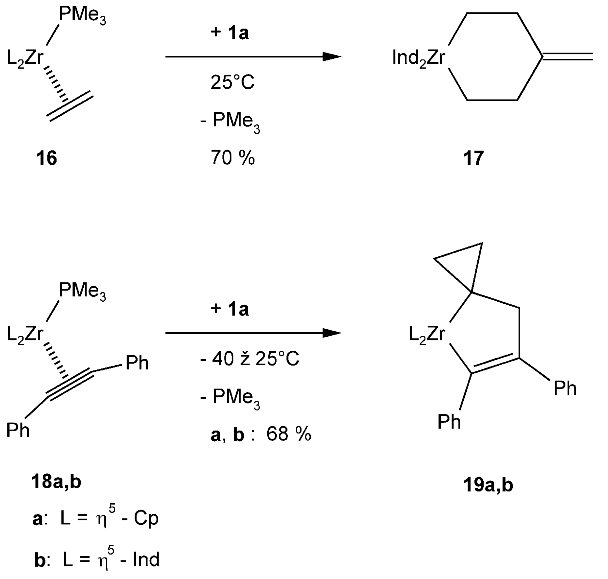
analogy to the behaviour of the titanium complex **8**, the reaction of **1a** with the zirconium complex **12a** affords the coupling product from two molecules of **1a** with the Cp_2Zr fragment; however, this reaction is no longer regioselective. Together with the zirconacyclopentane derivative **13** the zirconacyclopentane derivative **14** is formed in a ratio of 2:1 (combined yield 98%). Although the η^2-methylenecyclopropane complex initially formed by expulsion of 1-butene can be detected by spectroscopy (NMR) it cannot be isolated in pure form also not when one equivalent of **1a** is used. Surprisingly, on the other hand, the reaction of **1a** with the bis(η^5-indenyl)zirconium complex **12b** leads directly to the zirconacyclohexane complex **15**. No intermediates, such as a (η^2-methylenecyclopropane)zirconium complex or a zirconacyclopentane complex analogous to **13**, can be detected. This, like the observation that complex **13** cannot be transformed into a complex analogous to **15** on heating, suggests that **15** is formed directly through proximal ring opening of **1a** in the course of an oxidative [3+2] cycloaddition with a (η^2-methylenecyclopropane)zirconium complex (Scheme 4).

Two further examples for the differing behaviour of **1a** in coupling reactions with alkyne or alkene complexes of zirconocene and bis(η^5-indenyl)zirconium are provided by the reaction of the (η^2-ethene)bis(η^5-indenyl)zirconium complex **16** with **1a** and those between the (alkyne)zirconium complexes **18a**,**b** and **1a**. In the first case, bis(η^5-indenyl)-l-zircona-4-methylenecyclohexane (**17**) is formed exclusively via proximal ring opening of **1a** while, in the second case, the 1-zirconacyclopentene derivatives **19a** and **19b** are formed, also regioselectively, with the spiro-three-membered ring being in the vicinity of the metal (Scheme 5).

A comparable differentiation in reactivity is also found in the reactions of the benzylidenecyclopropane **1c** with **12a** and **12b**. On reaction with **1c** at room temperature, **12a** affords the benzylidenecyclopropane complex **20** which, upon warming at 60 °C for 18 h, rearranges to the 1-zircona-2-benzylidenecyclobutane complex **21a**. In contrast, the bis(η^5-indenyl)zirconium



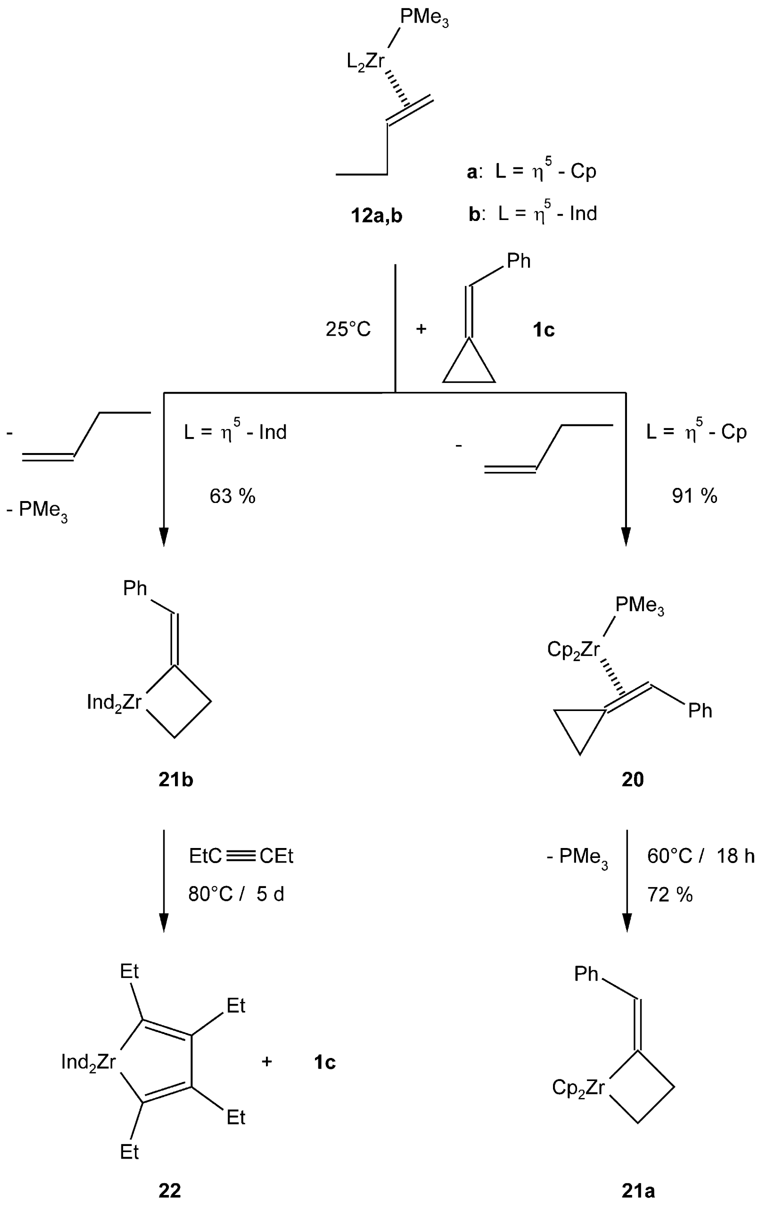
Scheme 4. Reactions of zirconium complexes **12a**,**b** with methylenecyclopropane **1a**.



Scheme 5. Different courses of the codimerisation of 1a with the zirconium-complexes **16** and **18a**,**b**.

complex **12b**, prepared in situ from $(\mathrm{lnd})_2ZrCl_2$, two equivalents of butyllithium and trimethylphosphane, also reacts with **1c** at room temperature but only to furnish the corresponding 1-zircona-2-benzylidenecyclobutane complex **21b**; intermediates such as, e.g. an olefin complex analogous to **20** can neither be isolated nor detected spectroscopically. An attempt to insert 3-hexyne into one of the two metalla carbon-5-bonds of **21b** to afford a 1-zirconabenzylidenecyclohexene analogous to **17** failed. Although a reaction was observed at 80 °C, **1c** was recovered and 3-hexyne reacted as previously observed to afford the known 1-zirconacyclopentadiene complex **22** [12] (Scheme 6).

The titanium and zirconium complexes described here for the first time possessed the calculated sum formulae, however, their molecular masses could rarely be determined by mass spectrometry. Even so the spectra did show characteristic fragmentation patterns. The structures were deduced from analyses of the NMR spectra. Thus, the ^{1}H- and ^{13}C-NMR spectra of the π-complexes **9a**, **9c** and **20** which are measured at low temperature to avoid rotation of the methylenecyclopropanes exhibit signals characteristic for a complexed double bond [15]. For example, the co-ordination shifts δ(complex)−δ(pure olefin) for **10a** amount to −5.12 (^{1}H) and −75–90 ppm (^{13}C). In contrast to the free olefin, the ^1J(C,H) coupling constants especially are appreciably reduced. As in the corresponding 1-alkene complexes of titanium and zirconium [11], the ligands are in a pseudotetrahedral arrangement about the metal. The methylenecyclopropanes lie in the plane defined by the



Scheme 6. Reactions of zirconium complexes **12a**,**b** with benzylidenecyclopropane **1c**.

M–PMe_3 bond and the olefin π-co-ordination axis. In contrast to the 1-alkene complexes, however, only one rotamer is formed in which the three-membered ring points in the opposite direction to the PMe_3 group. This is demonstrated by the differing coupling constants J(P,C1) and J(P,C4) (^{13}C), as well as the nuclear Overhauser difference spectrum [16] (e.g. saturation of the olefinic protons at C4 shows the adjacency to the PMe_3 group).

The 1-zircona-2-benzylidenecyclobutanes **21a** and **21b** were identified by comparison of their NMR spectra with those of 1-titana-2-methylenecyclobutanes [17]. The signals of the carbon atoms C(2) and C(4) directly bonded to the metal with ca. 210 and 43–59 ppm experience a shift to low field, while that for C(3) shows a high field shift typical for a metalla-four-membered ring(1.3–12.7 ppm) [18]. The values for the C=C double bond are practically unchanged and only one set of signals is observed for the C and H atoms of the cyclopentadienyl or indenyl units. The ^{1}H- and ^{13}C-NMR data for the two zirconacyclohexane derivatives **15** and **17** are in accord with the proposed structures (see Section 3) and are thus not discussed in detail here. H,H-COSY experiments support the assignments of the six multiplets of complex **15**.

The structure of complex **21b** in the solid state was additionally confirmed by X-ray crystallography. The results demonstrate a pseudotetrahedral arrangement with the indenyl ligands possessing a eclipsed *syn*-conformation. The angle between the metal and the midpoints of the two indenyl five-membered rings amounts to 136.5°, the zircona-four-membered ring is planar which deviation at C2 of 0.03 Å, the benzylidene C4 carbon atom is also in this plane while *ipso*-C atom of the phenyl ring cis to the zirconium in the four-membered ring is found to about 0.26 Å above this plane. Not only the length of the C=C double bond [1.35(1) Å] [17a] but also those of the C,C and Zr,C separations (see Fig. 1) are within the expected ranges [19]. As a result of the small size of the ring, C2 with a value of 2.59(1) Å has about the same bonding separation to zirconium as the C atoms in the indenyl five-membered rings.

In the present work, we have shown that although methylenecyclopropanes such as **1a** or **1c** preferentially participate in η^2-complexes over the C=C double bond with transition metal complexes, under certain circumstances-probably triggered by steric hindrance-they can also react through proximal opening of the three-membered ring. This leads to isolable 1-metalla-2-methylenecyclobutane derivatives such as the complexes **21a**,**b**. These compounds apparently do not occur during dimerisation reactions, instead a [3+2] cycloaddition with a η^2-bound unsaturated system takes place. Indications for this can be taken from the syntheses of the metallacyclohexane derivatives **15** and **17** in which there are no signs for the intermediate occurrence of a 1-metallacyclobutane. Furthermore, no further ring expansion of the isolated 1-metalla-2-methylenecyclobutanes by insertion of an unsaturated system can be achieved.

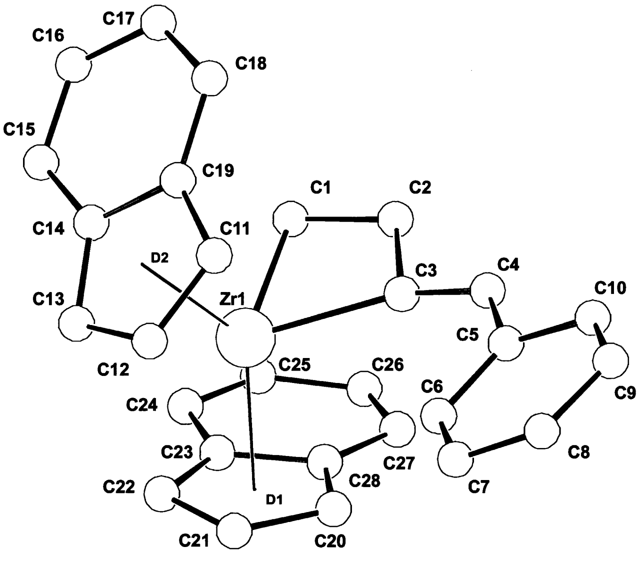


Fig. 1. Molecular structure of **21b**; selected bond lengths (Å) and angles (°); Zr–C1 2.18(1), Zr–C3 2.19(1), Zr–C2 2.59(1), Zr–C12 2.48(1), Zr–C13 2.49(1), Zr–C14 2.58(1), C1–C2 1.56(1), C2–C3 1.57(2), C3–C4 1.35(1); C1–Zr–C3 74.1(4), C2–C1–Zr 86.1(6),C1–C2–C3 114.3(8), C2–C3–Zr 85.5(6).

3. Experimental

The reactions were performed under argon in previously evacuated and baked-out Schlenk vessels. The solvents used were dried with Na–K alloy (pentane, hexane, toluene, [D_8]-THF) and MgH_2 (diethyl ether, THF) prior to distillation and stored under argon. Melting points were determined on a Gallenkamp apparatus. ^{1}H-, ^{13}C- and ^{31}P-NMR spectra were recorded on Bruker AC 200 FT and Bruker WH 400 FT instruments with TMS as internal standard or 85% H_3PO_4 as external standard. Mass spectra were recorded with MAT 311 APF and Finntgan MAT 95 spectrometers. Chemicals: *n*-butyllithium in hexane (1.6 M) (Deutsche Metallgesellschaft), titanocene dichloride (Aldrich) and zirconocene dichloride (Fluka) were used without further purification. Methylenecyclopropane **1a** [2a], Benzylidenecyclopropane **1c** [4], trimethylphosphane [20] Bis(trimethylphosphane)titanocene **8** [11a], (η^2-1-Butene) (trimethylphosphane) zirconocene [11a] were prepared by published procedures.

3.1. *(η^2-Methylenecyclopropane)(trimethylphosphane)titanocene (**9a**)*

To a solution of complex **8** (1.02 g, 3.1 mmol) in pentane (20 ml) is added at 0 °C a 0.32 M solution of **1a** in diethyl ether (9.62 ml, 3.1 mmol). After stirring for 1 h the solvent is evaporated (0.5 mbar, 20 °C) and the residue is washed once with pentane (5 ml). Compound **9a** is obtained as a red powder; yield 0.72 g (78%); m.p. (dec.) 103 °C. ^{1}H-NMR (400 MHz, [D_8]-THF, −80 °C): $\delta = 0.23$ (m, 2H, $J_{P,H} = 11.0$ Hz, =CH_2); 0.88 and 0.96 (m, 4H, ring-H); 1.32 (d, 9H, $J_{P,H} = 5.8$ Hz, PMe_3); 4.90 (d, 10H, $J_{P,H} = 2.4$ Hz, Cp). ^{13}C-NMR (75.5 MHz, [D_8]-THF, −110 °C): $\delta = 16.9$ (dq, $^1J_{C,H} = 128$, $J_{P,C} = 15.0$ Hz, PMe_3); 20.7 (t, $^1J_{C,H} = 156$ Hz, ring-C); 27.8 (dt, $^1J_{C,H} = 150$ Hz, $J_{C,P} = 20.6$ Hz, =CH_2); 40.5 (d, $J_{P,C} = 7.5$ Hz, ring-C); 101.4 (d, $^1J_{C,H} = 171$ Hz, Cp). ^{31}P-NMR (121.5 MHz, [D_8]-THF, −110 °C): $\delta = 26.5$. MS (70 eV): *m*/*z* (%) = [M^+] not observed, 232 (2) [M^+–PMe_3], 178 (100) [Cp_2Ti^+], 152 (8), 113 (21), 76 (14) [PMe_3^+], 61 (23) $C_{17}H_{25}PTi$ (308.2) Calc. C, 66.24; H, 8.18; P, 10.05; Ti, 15.53; Found: C, 66.24; H, 8.14; P, 10.11; Ti, 15.33%.

3.2. *(η^2-Benzylidenecyclopropane)(trimethylphosphane)titanocene (**9c**)*

To a solution of complex **8** (0.98 g, 3 mmol) in diethyl ether (25 ml) is added dropwise a solution of **1c** (0.85 g, 6.5 mmol) in ether (10 ml) at room temperature (r.t.). The solution turns red and during 1 h stirring a reddish–brown solid precipitates which is filtered off, washed twice with pentane (3 ml) and dried under vacuum (0.5 mbar); yield 0.96 g (76%), m.p. (dec.) 129 °C. ^{1}H-NMR

(400 MHz, [D_8]-THF, −80 °C): $\delta = 0.47$ (d, 3H, $J_{P,H} = 5.3$ Hz, PMe$_3$); [0.83, 1.16, 1.21, 1.45 (m, 4H, ring-H)]; 1.28 (d, 3H, $J_{P,H} = 6.6$ Hz, PMe$_3$); 1.59 (d, 3H, $J_{P,H} = 6.2$ Hz, PMe$_3$); 1.79 (d, 1 H, $J_{P,H} = 8.8$ Hz); [4.94 (d, 5H, $J_{P,H} = 2.4$Hz, Cp); 5.10 (d, 5H, $J_{P,H} = 2.2$ Hz, Cp)]; [6.47, 7.57 (2H, *o*-phenyl)]; [6.59, 7.32 (2H, *m*-pheny)]; 6.88 (1H, *p*-phenyl). ^{13}C-NMR (75.5 MHz, [D_8]-THF, −80 °C): $\delta = 14.3$ (dq, $^1J_{C,H} = 128$ Hz, $J_{P,C} = 14.6$ Hz, PMe$_3$); 16.7 (dq, $^1J_{C,H} = 128$ Hz, $J_{P,C} = 18.9$ Hz, PMe$_3$); 18.5 (dq, $^1J_{C,H} = 124$ Hz, $J_{P,C} = 8.8$ Hz, PMe$_3$); [21.3 (t, $^1J_{C,H} = 156$ Hz); 22.1 (t, $^1J_{C,H} = 156$ Hz), C-ring]; 48.6 (dd, $^1J_{C,H} = 145$ Hz, $J_{P,C} = 15.2$ Hz, =CH); 48.8 (d, $J_{P,C} = 9.6$ Hz, $>$C=C); 103.8 and 104.1 (d, $^1J_{C,H} = 171$ Hz, Cp); 119.7 (d, $^1J_{C,H} = 158$ Hz, *p*-phenyl); 123.5 (d, $^1J_{C,H} = 156$ Hz, *o*-phenyl), 129.0 (d, $^1J_{C,H} = 153$ Hz, *o*-phenyl); 127.5 and 127.7 (d, $^1J_{C,H} = 154$ Hz, *m*-phenyl); 154.5 (d, $J_{P,C} = 3.4$ Hz, *ipso*-phenyl). ^{31}P-NMR (121.5 MHz, [D_8]-THF, −80 °C): $\delta = 20.8$. $C_{23}H_{29}PTi$ (383.2) Calc. C, 71.80; H, 7.55; P, 8.06; Ti, 12.47; Found: C, 71.69; H, 7.59; P, 8.26; Ti, 12.26%.

3.3. (η^2-Benzylidenecyclopropane)(trimethylphosphane) zirconocene (20)

To a solution of complex **12a** (0.91 g, 2.23 mmol) in diethyl ether (25 ml) at r.t. is added dropwise a solution of **1c** (0.64 g, 4.9 mmol) in diethyl ether (10 ml). During the addition of **1c**, **20** begins to precipitate as a yellow, microcrystalline solid. After additional 1 h stirring, the solid is filtered, washed three times with pentane (3 ml) and dried at 0.5 mbar to leave **20**; yield 0.87 g (91%), m.p. 133 °C (decomp.). ^{1}H-NMR (400 MHz, [D_8]-THF, −80 °C): $\delta = 1.14$ (d, 9H, $J_{P,H} = 6.1$ Hz, PMe$_3$); 1.44 (d, 1H, $J_{P,H} = 5.3$ Hz, =CHPh); [5.28 (d, 5H, $J_{P,C} = 1.5$Hz); 5.43 (d, 5H, $J_{P,C} = 1.4$ Hz), Cp]; 6.43 (1 H, *p*-phenyl); 6.46 and 6.78 (*o*-phenyl), 6.92 and 6.78 (*m*-phenyl). ^{13}C-NMR (75.5 MHz, [D_8]-THF, −80 °C): $\delta = 15.6$ (bm, PMe$_3$); 20.0 (t, $^1J_{C,H} = 155$ Hz, three-membered ring); 23.3 (t, $^1J_{C,H} = 156$ Hz, three-membered ring); 36.1 (d, $J_{P,C} = 8.4$ Hz, $>$C=CHPh); 42.4 (dd, $J_{C,H} = 140$ Hz, $J_{P,C} = 10.5$ Hz, $>$C=CHPh); 104.5 and 105.4 (d, $^1J_{C,H} = 170$ Hz, Cp); 117.7 (d, $^1J_{C,H} = 158$ Hz, *p*-phenyl); 122.7 and 126.9 (d, $^1J_{C,H} = 153$ Hz, *o*-phenyl); 127.4 and 127.6 (d, $^1J_{C,H} = 154$ Hz, *m*-phenyl); 156.6 (d, $J_{P,C} = 2.6$ Hz, *ipso*-phenyl). ^{31}P-NMR (121.5 MHz, [D_8]-THF, −80 °C): $\delta = 3.3$. MS (70 eV): *m/z* (%) = [M$^+$] not observed, 350 (8) [M$^+$−PMe$_3$], 220 (100) [Cp$_2$Zr^4], 194 (10), 76 (16) [PMe$_3^+$], 61 (23). $C_{23}H_{29}PZr$ (427.7) Calc. C, 64.59; H, 6.83; P, 7.24; Zr, 21.33; Found: C, 64.51; H, 6.85; P, 7.29; Zr, 21.31%.

3.4. Bis(η^5-cyclopentadienynl-1-zircona-2-benzylidenecyclobutane (21a)

A solution of complex **20** (4.0 g, 9.3 mmol) in THF (30 ml) is heated at 60 °C for 18 h. The solvent is removed in vacuum (0.5 mbar) and the oily residue redissolved in diethyl ether (20 ml). After 3 days at −20 °C, unreacted **20** has precipitated as a yellow solid, which is filtered off. The volume of the mother liquid is reduced to 10 ml. After 10 days at −20 °C, orange crystals have been precipitated which are filtered off and dried in vacuum to leave **21a**; yield 2.3 g (70%), m.p. (dec.) 125 °C. ^{1}H-NMR (200 MHz, [D_8]-THF, 25 °C): $\delta = 0.99$ (m, 2H, 3-H); 1.80 (m, 2H, 4-H); 5.94 (s, 10H, Cp); 7.52 (m, 1H, 5-H); 7.0–7.4 (m, 5H, phenyl). ^{13}C-NMR (50.3 MHz, [D_8]-THF, 25 °C): $\delta = 1.3$ (t, $^1J_{C,H} = 137$ Hz, C-3); 43.4 (t, $^1J_{C,H} = 137$ Hz, C-4); 108.7 (d, $^1J_{C,H} = 170$ Hz, Cp); 126.0 (d, $^1J_{C,H} = 160$ Hz, *p*-phenyl); 126.4 (d, $^1J_{C,H} = 157$ Hz, *o*-phenyl); 128.5 (d, $^1J_{C,H} = 158$ Hz, *m*-phenyl); 143.1 (s, *ipso*-phenyl); 137.2 (d, $^1J_{C,H} = 145$ Hz, C-5); 212.2 (s, C-2). MS (70 eV): *m/z* (%) = 350 (6.6) [M$^+$], 322 (13.3) [M$^+$ −28], 220 (100) [Cp$_2$Zr$^+$]. $C_{20}H_{20}Zr$ (351.6) Calc. C, 68.32; H, 5.73; Found: C, 68.26; H, 5.84%.

3.5. Bis(η^5-indenynl)-1-zircona-2-benzylidenecyclobutane (21b)

At −78 °C a 1.6 M solution of *n*-butyllithium in hexane (4.9 ml, 7.9 mmol) is added dropwise to a suspension of bis(η^5-indenyl)zirconium dichloride (1.5 g, 3.9 mmol) in THF (80 ml). After stirring for 1 h **1c** (0.8 ml, 6.1 mmol) and trimethylphosphane (0.5 ml, 4.8 mmol) are added and the whole mixture is slowly warmed to r.t. After stirring for another 15 h the solvent is removed at 0.5 mbar and the residue extracted over celite with toluene (25 ml). The toluene is evaporated at 0.5 mbar per 25 °C and the residue dissolved in diethyl ether. After cooling at −78 °C for 2 days a yellow microcrystalline solid has precipitated, which is filtered and dried in vacuum (0.5 mbar) to leave pure **21b** as a yellow powder; yield 1.1 g (63%). Crystals suitable for an X-ray analysis were obtained by recrystallisation from diethyl ether–THF (3:1). ^{1}H-NMR (200 MHz, [D_8]-THF, 25 °C): $\delta = -0.98$ (m, 2H, 4-H); 0.31 (m, 2H, 3-H); 6.00 (t, 2H, $^3J_{H,H} = 2.7$ Hz, indenyl); 6.24 (d, 4H, $^3J_{H,H} = 2.7$ Hz, indenyl); 6.96 (m, 4H, indenyl); 7.30 (m, 4H, indenyl); 7.0–7.2 (m, 5H, phenyl); 7,41 (m, 1 H, 5-H). ^{13}C-NMR (50.3 MHz, [D_8]-THF, 25 °C): $\delta = 12.7$ (t, $^1J_{C,H} = 137$ Hz, C-3); 59.5 (t, $^1J_{C,H} = 139$ Hz, C-4); 136.4 (d, $^1J_{C,H} = 147$ Hz, C-5); 210.5 (s, C-2); [95.5 (d, $^1J_{C,H} = 174$ Hz); 99.3 (d, $^1J_{C,H} = 176$ Hz); 111.8 (d, $^1J_{C,H} = 169$ Hz); 123.7 (s); 123.8 (s); 124.1 (d); 124.4 (d); 125.5 (d), indenyl]; 126.3 (d, $^1J_{C,H} = 150$ Hz, *m*-phenyl); 127.0 (d, $^1J_{C,H} = 146$ Hz, *p*-phenyl); 128.9 (d, $^1J_{C,H} = 158$ Hz, *o*-phenyl); 143.0 (s, *ipso*-phenyl). MS (70 eV): *m/z* (%) = 450 (0.7) [M$^+$], 422 (4.2) [M$^+$ −28], 320 (100) [indenyl$_2$Zr$^+$]. $C_{28}H_{24}Zr$ (451.7) Calc. C, 74.45; H, 5.36; Found: C, 74.28; H, 5.39%.

3.6. *Bis(η^5-cyclopentadienynl-4-titanadispiro[2.2.2.1]nonane (**10**)*

Complex **9a** (0.7 g, 2.27 mmol) is suspended in pentane (10 ml) and diethyl ether (30 ml) at 0 °C and **1a** (0.25 g, 4.5 mmol) added. After 1 h stirring, a clear red solution is obtained. After warming to r.t., the solvent is evaporated and the residue resolved in pentane–ether (20 ml, 1:1). Some impurities are filtered over celite and the red filtrate is cooled to −20 °C. After 5 days red crystals are obtained which are filtered and dried in vacuum (0.5 mbar); yield 0.36 g (56%) **10**; m.p. (dec.) 76 °C. ^{1}H-NMR (200 MHz, [D_8]-THF, 25 °C): $\delta = -0.08$ (ddd, $^3J_{H,H} = 9.3$ and 4.9 Hz, $^2J_{H,H} = -3.3$ Hz, 2′-H and 3′-H); 0.02 (ddd, $^3J_{H,H} =$ 9.1 and 5.5 Hz, $^2J_{H,H} = -3.4$ Hz, 7′-H and 8′-H); 0.12 (ddd, 7-H and 8-H); 0.20 (ddd, 2-H and 3-H); 0.98 (s, 9-H); 1.34 (s, 5-H); 6.23 (s, Cp). ^{13}C-NMR (75.5 MHz, [D_8]-THF, −30 °C): $\delta = 15.8$ (t, $^1J_{C,H} = 158$ Hz, C-7 and C-8); 19.8 (t, $^1J_{C,H} = 154$ Hz, C-2 and C-3); 24.9 (s, C-6); 49.6 (s, C-1); 52.6 (t, $^1J_{C,H} = 124$ Hz, C-9); 59.4 (t, $^1J_{C,H} = 128$ Hz, C-5); 115.7 (d, $^1J_{C,H} = 173$ Hz, Cp). MS (70 eV): m/z (%) = [M$^+$] not observed, 178 (100) [Cp_2Ti^+], 113 (10). $Ci_8H_{22}Ti$ (286.3) calcd. C 75.51, H 7.75, Ti 16.72; Found: C, 74.98; H, 8.02; Ti, 16.59%.

3.7. *Bis(η^5-cyclopentadienyl)-4-zirconadispiro[2.2.2.1]nonane (**13**) and Bis(η^5-cyclopenta-dienyl)-4-zirconadispiro[2.1.2.2]nonane (**14**)*

To a solution of complex **12a** (1.55 g, 4.4 mmol) in diethyl ether (25 ml) is added dropwise a solution of **1a** (1.18 g, 22 mmol) in diethyl ether (20 ml) at 0 °C. After stirring at 0 °C for 1 h the solution is warmed to r.t. Small impurities are removed by filtration over celite and the filtrate is evaporated to dryness. This leaves a mixture of the complexes **13** and **14** in a ratio of 2:1 (determined by integration of ^{1}H-NMR Cp signals) as a yellow powder; yield 1.43 g (98%). The following NMR data were determined from the 2:1 mixture of **13/14**. **13**: ^{1}H-NMR (200 MHz, C_6D_6, 25 °C): $\delta = 0.38$ (ddd, $^3J_{H,H} = 8.6$ and 4.7 Hz, $^2J_{H,H} = -2.9$ Hz, 2′-H, 3′-H and 8′-H); 0.45 (ddd, 2-H and 3-H); 1.05 (s, 9-H); 1.12(s, 5-H); 5.89 (s, Cp). ^{13}C-NMR (75.5 MHz, [D_8]-THF, 25 °C): $\delta = 17.1$ (t, $^1J_{C,H} = 159$ Hz, C-2 and C-3); 18.0 (t, $^1J_{C,H} = 158$ Hz, C-7 and C-8); 20.4 (s, C-6); 35.4 (s, C-1); 45.9 (t, $^1J_{C,H} = 124$ Hz, C-9); 50.6 (t, $^1J_{C,H} = 124$ Hz, C-5); 112.6 (d, $^1J_{C,H} = 172$ Hz, Cp). **14**: ^{1}H-NMR (200 MHz, C_6D_6, 25 °C): $\delta = 0.38$ (ddd, $^3J_{H,H} = 8.6$ and 4.7 Hz, $^2J_{H,H} = -2.9$ Hz, 2′-H, 3′-H, 6′-H and 7′-H); 0.46 (ddd, 2-H, 3-H, 6-H and 7-H); 1.36 (m, 8-H and 9-H); 5.84 (s, Cp). ^{13}C-NMR (75.5 MHz, [D_8]-THF, 25 °C): $5 = 18.6$ (t, $^1J_{C,H} = 157$ Hz, C-2, C-3, C-6 and C-7), 35.4 (s, C-1 and C-5), 41.7 (t, $^1J_{C,H} = 126$Hz, C-8 and C-9), 113.7 (d, $^1J_{C,H} = 173$ Hz, Cp). MS (70 eV): m/z (%) = [M$^+$] not observed, 220 (100) [Cp_2Zr^+], 194 (8). $C_{18}H_{22}Zr$ (329.6) Calc. C, 65.59; H, 6.67; Zr, 27.68; Found: C, 65.39; H, 6.75; Zr, 27.96%.

3.8. *Bis(η^5-indenyl)-4-zircona-7-methylenespiro[2.5]octane (**15**)*

To a suspension of bis(η^5-indenyl)zirconium dichloride (0.97 g, 2.47 mmol) in THF (70 ml) at −78 °C is added a 1.6 M solution of butyllithium in hexane (3.2 ml, 5.12 mmol). After 1 h stirring, trimethylphosphane (0.5 ml, 4.8 mmol) and **1a** (1 ml, 11 mmol) are added. The reaction mixture is warmed to r.t. and stirred at this temperature for 12 h. All volatile materials are removed at 0.5 mbar and the oily residue is taken up in toluene (20 ml). Insoluble material is removed by filtration over celite and the solvent distilled off. The residue is taken up in ether (2 ml) and pentane (10 ml) added. The hereby formed colourless precipitate is filtered off and the filtrate cooled to −78 °C. After 1 month, an ochre-coloured powder has precipitated, which is filtered and dried in vacuum to afford **15**; yield 1.06 g (58%), m.p. (dec.) 157 °C. ^{1}H-NMR (200 MHz, [D_8]-THF, 25 °C): $\delta = -1.25$ (m, 2H, 5-H); 0.09 and 0.59 (m, 4H, 2-H and 3-H); 1.82 (s, 2H, 8-H); 2.46 (m, 2H, 6-H); 4.15 (m, 2H, 9-H); [5.68 (m, 2H); 6.02 (m, 2H); 6.21 (m, 2H); 7.1 1 (m, 4H); 7.26 (m, 2H); 7.60 (m, 2H); indenyl]. ^{13}C-NMR (50.3 MHz, [D_8]-THF, 25 °C): $\delta = 17.6$ (t, $^1J_{C,H} = 157$ Hz, C-2 and C-3); 41.6 (t, $^1J_{C,H} = = 122$ Hz, C-6); 45.0 (s, C-1); 55.8 (t, $^1J_{C,H} = 123$ Hz, C-8); 60.0 (t, $^1J_{C,H} =$ 120 Hz, C-5); 107.2 (t, $^1J_{C,H} = 154$ Hz, C-9); 155.0 (s, C-7); [100.9 (d, $^1J_{C,H} = 173$ Hz); 104.0 (d, $^1J_{C,H} = 173$ Hz); 118.7 (d, $^1J_{C,H} = 170$ Hz); 125.0 (d); 125.3 (d); 125.5 (d); 125.8 (s); indenyl]. $C_{26}H_{26}Zr$ (429.7) Calc. C, 72.67; H, 6.10; Found: C, 72.65; H, 6.08%.

3.9. *Bis(η^5-indenyl)-1-zircona-4-methylenecyclohexane (**17**)*

To a suspension of complex **16** (0.49 g, 1.15 mmol) in THF (10 ml) is added at −78 °C a 1.87 M solution of **1a** (0.62 ml, 1.16 mmol) in diethyl ether (10 ml). The reaction mixture is warmed to r.t. and stirred at this temperature for 6 h whereby a green solution is formed. The solvents are removed at 0.5 mbar and the oily residue is taken up in diethyl ether (2.5 ml). After 2 weeks a yellow–green solid has precipitated from which the solvent is decanted. After drying at 0.5 mbar **17** is obtained as a powder; yield 0.32 g (70%), m.p. (dec.) 73 °C. ^{1}H-NMR (200 MHz, [D_8]-THF, 25 °C): $\delta = -0.6$ (m, 4H, 2-H and 6-H); 2.4 (m, 4H, 3-H and 5-H); 4.1 (s, 2H, *exo*-CH$_2$); [5.9 (t, 2H, $^3J_{H,H} = 3.3$ Hz); 6.0 (d, 4H); 7.1 (m, 4H); 7.3 (m, 4H); indenyl]. ^{13}C-NMR (50.3 MHz, [D_8]-THF, 25 C): $\delta = 41.4$ (t, $^1J_{C,H} = 125$ Hz, C-3 and C-4); 55.7 (t, $^1J_{C,H} = 119$ Hz, C-2 and C-6); 107.6 (t, $^1J_{C,H} = 153$ Hz, *exo*-CH$_2$); 157.2 (s, C-4); [101.1 (d, $^1J_{C,H} = 174$ Hz); 117.9 (d, $^1J_{C,H} = 170$ Hz); 124.9 (s);

125.0 (d, $^1J_{C,H} = 170$ Hz); 125.3 (d, $^1J_{C,H} = 160$ Hz); indenyl]. MS (70 eV): m/z (%) = 402 (1.6) [M^+], 320 (100) [Ind_2Zr^+]. $C_{24}H_{24}Zr$ (403.7) calcd. C 71.41, H 5.99; Found: C, 71.55; H, 6.03%.

3.10. Bis(η^5-cyclopentadienyl)-5,6-diphenyl-4-zirconaspino [2,4]hept-5ene (**19a**)

To a solution of complex **18a** (0.52 g, 1.1 mmol) im THF (5 ml) is added at 0 °C **1a** (0.26 g, 5 mmol). After 1 h stirring at r.t. THF is removed at 0.5 mbar and the yellow solid residue suspended in pentane (15 ml), filtered and dried at 0.5 mbar to yield 0.35 g (68%) of complex **19a**; m.p. (dec.) 152 °C. ^{1}H-NMR (200 MHz, [D_8]-toluene, 25 °C): $\delta = 0.47$ (m, 2H;$J_{H,H} = 3.1$, 8.0 4,9, 8.8, trans 2-H and 3-H); 0.62 (m, 2H, *cis* 2-H and 3-H); 2.29 (s, 2H, 7-H); 5.89 (s,10H,C_p), 6.58(m, 4H, phenyl); 7.0 (m, 6H, penyl). ^{13}C-NMR (75.5 MHz, [D_8]-THF, −30 °C) $\delta = 19.3$ (t, $^1J_{C,H} = 156$ HZ, (C-2 and C-3); 40.5 (s, C-1); 49.8 (t, $^1J_{C,H} = 124$ HZ; 113.5 (d, $^1J_{C,H} = 172$Hz Cp); 144,2 (s, C-6); 186.1 (s, C-5); [145,1 (s), 150.9(s), 127.3(d), 127.8(d), 122.9(d), 125,7(d), 128.3(d), 129.6(d) phenyl). MS(70 eV): m/z (%) = 452(8) [M^+], −220(100)[Cp_2Zr^+]. $C_{28}H_{26}Zr$(453.7) Calc. C, 74.12; H, 5.78; Zr, 20.10; Found: C, 74.14; H, 5.78; Zr, 20.25%.

3.11. Bis(η^5-indenyl)-5,6-diphenyl-4-zirconaspiro[2.4]hept-5-ene (**19b**)

To a solution of complex **18b** (0.62 g, 1.08 mmol) in toluene (6 ml) is added at −40 °C an excess of **1a** (1 ml, 7 mmol). The yellow solution is warmed to r.t., stirred for 4 days in a closed vessel, then the solvent is evaporated at 0.5 mbar. The oily residue is taken up in pentane (8 ml) and stirred for some hours whereby **19** precipitates as a yellow powder which is filtered off and dried in vacuum (0.5 mbar); yield 0.47 g (79%), m.p. (dec.) 110 °C. ^{1}H-NMR (200 MHz, [D_8]-THF, 25 °C): $\delta = 0.29$ (m, 2H, *trans* 2-H and 3-H); 0.70 (m, 2H, *cis* 2-H and 3-H); 2.05 (s, 2H, 7-H); 6.03 (m, 4H, indenyl); 6.10 (t, $^3J_{H,H} = 3.6$ Hz, indenyl); 6.3–7.4 (m, 18H, phenyl). ^{13}C-NMR (50.3 MHz, [D_8]-THF, 25 °C): $\delta =$ 20.6 (t, C-2 and C-3); 43.7 (s, C-1); 51.8 (t, C-7); 145.6 (s, C-6); 188.2 (s, C-5); [103.1 (d); 104.3 (d); 121.7 (d); indenyl]. $C_{36}H_{30}Zr$ (553.8) Calc. C, 78.07; H, 5.46; Zr, 16.47; Found: C, 77.89; H, 5.48; Zr, 15.75%.

Crystal structure analysis of **21b**; crystal data: $C_{28}H_{24}Zr, M_r = 451.71$ g mol^{-1}, orthorhombic space group *Pbca* (no. 61), $a = 14.632(3)$, $b = 6.636.4709(3)$, $c = 16.989(2)$ Å, $V = 4135.4(1)$ Å^3, $Z = 8$, $d_{calcd} = 1.451$ Mg m^{-3} Data Collection; data were collected with an Enraf Nonius CAD-4 diffractometer at 100 K. Crystal size 0.9 × 0.28 × 0.21 mm, range for data collection $2.21 < \theta < 28.06°$, $\lambda = 0.71069$ Å, Mo–K$_\alpha$ (graphite monochromator), $0 < h < 18.0 < 22.0 < l < 21$, 4631 [$R_{int} = 0.0420$] independent reflections, collected reflection 5152, of which 3647 were considered, observed with $I > 2\sigma(T)$. Structure solution and refinement: the structure was solved using direct methods (SHELX-86 [21] and refined with the full-matrix least-squares procedure against F^2 (SHELX-93) [22], the anisotropic refinement converged at $R_1 = 0.082$ and $R_w = 0.155$.

4. Supplementary material

Crystallographic data (excluding structure factors) for **21b** have been deposited with the Cambridge Crystallographic Data centre as supplementary publication no. CCDC-177976. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www; http://www.ccdc.cam.ac.uk)

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