Bicyclic carbo- and heterocycles from an allylidene complex and cyclic 1,3-dienes by tandem cyclopropanation/Cope rearrangement

Helmut Fischer* and Thomas Froneck

Fakultät für Chemie, Universität Konstanz, Postfach 5560 M727, D-78434 Constance (Germany)

(Received January 19, 1994)

Abstract

The allylidene complex $(CO)_5W{=}CH{-}C(Ph){=}C(Ph)H$ (**4**) reacts with cyclopentadiene by stereospecific transfer of the carbene ligand to one of the two double bonds of cyclopentadiene to give a *cis*-divinylcyclopropane complex **5**. The divinylcyclopropane ligand coordinates to the metal via the unsubstituted double bond. Addition of bromide to solutions of **5** gives rise to the formation of $[(CO)_5WBr]^-$ and a bicyclo[3.2.1]octadiene (**6**), the Cope rearrangement product of the free divinylcyclopropane. Thermolysis of **5** affords **6** and its $(CO)_5W$ complex. The reaction of **4** with furan (**8a**), 2-methylfuran (**8b**) and 3-methylfuran (**8c**) affords the $(CO)_5W$(bicyclo[3.2.1]oxaheptadiene) complexes (**9a–c**). The formation of **9a–c** which is chemo-, regio- and stereospecific is explained by a tandem cyclopropanation/Cope rearrangement sequence. The bicyclic ligands **10a–c** are liberated from the metal either by thermolysis of solutions of **9a–c** or by addition of bromide.

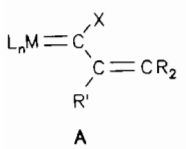
Key words: Cyclopropanation; Tungsten complexes; Allylidene complexes; Cope rearrangement; Bicyclo[3.2.1]octadiene; Bicyclo[3.2.1]oxaheptadiene; Divinylcyclopropane complexes

Introduction

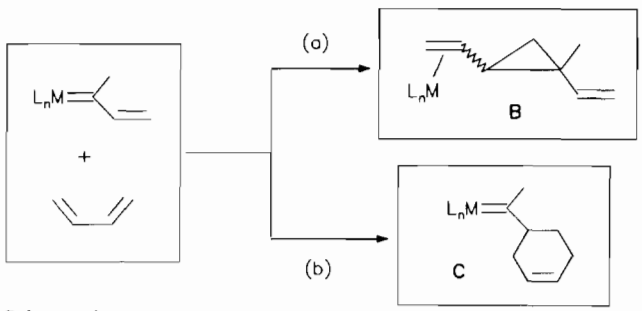
Allylidene complexes (vinylcarbene complexes, 1-metallabuta-1,3-dienes) have been postulated as intermediates in several stoichiometric or catalytic reactions. Examples include the formation of naphthols and other organic products from the reaction of alkynes with chromium carbene complexes [1, 2] and the polymerization of alkynes [3]. Theoretical investigations indicate that the coupling of a coordinated alkyne with the carbene ligand in carbene complexes is one of the key steps in the Dötz reaction [4].

In mononuclear complexes the allylidene ligand can coordinate to the metal either in an η^1- or an η^2-fashion. A great number of low-valent heteroatom-stabilized η^1-allylidene complexes **A** (X = OR, NR_2) have been prepared and their reactivity has been studied in some detail. With donor- or acceptor-substituted olefins vinylcyclopropanes from the transfer of the carbene ligand to the C=C bond of the olefins or products derived thereof have been obtained [5]. In the reactions with conjugated dienes two different paths were observed: cyclopropanation (Scheme 1: path (a)) and [4+2]cycloaddition (path (b)).

Generally allylidene(pentacarbonyl) complexes ($L_nM = M(CO)_5$) react with 1,3-dienes by path (b) giving Diels–Alder products [5a, 6]. An exception is the reaction of pentacarbonyl[cyclohexenyl(methoxy)carbene]-chromium with $MeO(H)C{=}CH{-}C(OR'){=}CH_2$ (R' = $SiMe_2Bu$, $SiMe_3$) which affords the corresponding *trans*-divinylcyclopropanes and bicyclo[5.4.0]undecane deriv-



A



Scheme 1.

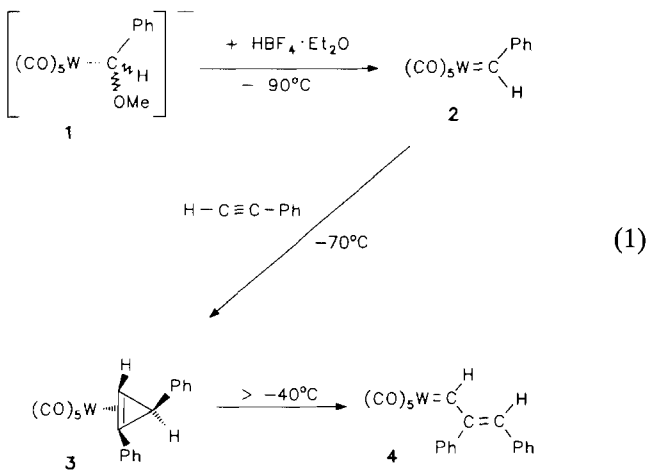
*Author to whom correspondence should be addressed.

SSDI 0020-1693(94)03885-R

atives. The undecane is proposed to result from a *cis*-divinylcyclopropane intermediate by Cope rearrangement [5a, 6].

In contrast to heteroatom-stabilized allylidene complexes low-valent non-heteroatom-stabilized allylidene complexes are rather rare. $[Cp(CO)_2Fe{=}CH{-}CH{=}CMe_2]^+$ which can be prepared by protonation of $Cp(CO)_2Fe{-}CH{=}CH{-}CMe{=}CH_2$ [7] or by proton-induced OH^--abstraction from $Cp(CO)_2Fe{-}CH{=}CH{-}C(OH)Me_2$ [8] reacts with olefins by carbene transfer to form cyclopropanes. There is no report on the reactions with dienes.

We recently observed that certain allylidene(pentacarbonyl)tungsten complexes are accessible by a novel high-yield tandem C,C-coupling/rearrangement reaction (eqn. (1)) [9]: the reaction of the α-methoxybenzyl(pentacarbonyl)tungstate (**1**) [10] with $HBF_4 \cdot Et_2O$ affords the benzylidene complex **2** [11]. Addition of phenylacetylene to **2** gives the cyclopropene complex **3** by coupling of the carbene ligand with the C≡C bond of the alkyne. At temperatures higher than −35 °C, **3** rearranges stereoselectively to form the allylidene complex **4** [9].



(1)

We now report on the reaction of **4** with cyclic 1,3-dienes to give (i) an isolable *cis*-divinylcyclopropane complex, (ii) a bicyclo[3.2.1]octadiene derivative, (iii) several bicyclo[3.2.1]oxaheptadienes as well as (iv) their pentacarbonyltungsten complexes.

Experimental

General comments

All reactions and manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk line techniques. The solvents were carefully dried (CaH_2, Na) and distilled before use. Silica gel used in column chromatography (Merck No. 60, 0.082–0.2 mm) was dried at 100 °C for several hours, then degassed several times and stored under nitrogen. Preparative thin layer chromatography was carried out using silica gel plates (Merck F_{254}, 1 or 2 mm). The melting points are uncorrected. Yields refer to purified compounds and are not optimized.

IR spectra: Bio-Rad FTS60 spectrophotometer; ^1H and ^{13}C NMR spectra: Bruker WM 250 and AC 250 instruments; mass spectra: Varian MAT 112S (EI, 70 eV); UV–Vis: Hewlett-Packard 8452A diode-array spectrophotometer. 3-Methylfuran [12] and benzylidene(pentacarbonyl)tungsten [11] were prepared according to literature procedures. Cyclopentadiene was obtained from dicyclopentadiene by distillation. All other chemicals were commercial products and were used as supplied.

(1) Generation of 4

$NEt_4[(CO)_5W{-}C(Ph)(H)OMe]$ (**1**) (2.00 g, 3.48 mmol) was dissolved in 25 ml of dichloromethane and 1 ml of $HBF_4 \cdot Et_2O$ was rapidly added at −100 °C while vigorously stirring the solution. The yellow solution immediately turned deep red. After 1 min 25 ml of pentane cooled to −80 °C were added. The solution was filtered at −80 °C over *c.* 15 cm of silica gel using a protecting glass frit. The silica gel was eluted with 150 ml of pentane/dichloromethane (1:1) precooled to −80 °C. The solvent of the combined filtrates was then removed *in vacuo* at −70 °C and the residue recrystallized from pentane. At −70 °C the residue (**2**) was dissolved again in 20 ml of dichloromethane and 3.65 mmol of phenylacetylene were added. The solution was warmed to −30 °C. After 30 min at −30 °C the solution predominantly consisted of **4** and a minor amount of $(CO)_5W$[2,3-diphenylcyclopropene] (**3**) and was used for the subsequent reactions with dienes.

(2) Pentacarbonyl{2,3-η^2-[endo-(1',2'-diphenylvinyl)-bicyclo[3.1.0]hex-2-en]}tungsten (5)

5 ml of cyclopentadiene were added to the solution of **4** (see (1)). Within 12 h at −30 °C the colour of the solution changed to red-brown. Solvent and excess cyclopentadiene were removed *in vacuo*. The residue was redissolved in pentane and chromatographed on silica gel using pentane/CH_2Cl_2 (5:1) as the eluant. The light yellow band was eluted and the solvent removed *in vacuo* at −30 °C to give a yellow powder. Yield 1.1 g (54% based on **1**). M.p. 88 °C (dec.).

The numbering scheme for the atoms is given in Fig. 1. IR (n-pentane): ν(CO) 2079w, 1961s, 1948vs cm^{-1}. ^1H NMR ($CDCl_3$, −45 °C): 1.76 (m, C5–H), 2.50 (m, C6–H), 2.66 (m, C1–H), 2.95 (s, CH_2), 4.40 (d, 3.8 Hz, C3–H), 4.66 (d, 4.6 Hz, C2–H), 6.52 (d, 1.8 Hz, C8–H), 7.0–7.4 (m, Ph). ^{13}C NMR ($CDCl_3$, −45 °C): 21.5 (C5), 34.1, 34.3, 35.3 (C1, C4, C6), 85.5 (C3), 88.8 (C2), 126.7, 127.1, 127.9, 128.1, 128.5, 129.0 (C_o, C_m, C_p),

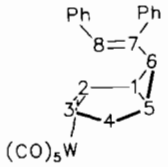


Fig. 1. Numbering scheme for the carbon atoms in **5**.

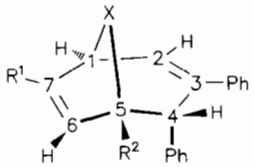


Fig. 2. Numbering scheme for the carbon atoms in **6** (X = CH_2), **10** and the ligand in **9** (X = O).

132.5, 134.1, 136.6, 139.9 (C_{ipso}, C7, C8), 196.9 (*cis*-CO), 201.8 (*trans*-CO). MS *m/z* [%]: 582 [1, M^+], 442 [6, $M^+ - 5CO$], 258 (100, $M^+ - W(CO)_5$]. *Anal.* Calc. for $C_{25}H_{18}O_5W$: C, 51.57; H, 3.12. Found: C, 50.73; H, 3.18%.

(3) 3-endo-4-Diphenyl-bicyclo[3.2.1]octa-2,6-diene (6)

A solution of 240 mg (0.4 mmol) (**4**) and 6.5 g NEt_4Br in 20 ml of dichloromethane was stirred for 15 h at room temperature. The solvent was removed *in vacuo* and the residue was extracted three times with 25 ml of Et_2O each. The solvent was removed *in vacuo* and the yellow oily residue was purified by thin layer chromatography (eluant: pentane/CH_2Cl_2 5:1; R_f of **6**: 0.56). Colourless crystals. Yield 65 mg (61%). M.p. 53 °C.

The numbering scheme for the carbon atoms in **6**, **9** and **10** is given in Fig. 2. ^{1}H NMR ($CDCl_3$, r.t.): 1.99 (d, 9.5 Hz, C8–H_{syn}), 2.15 (m, C6–H_{anti}), 2.89 (ddd, 6.7, 4.6, 2.8 Hz, C1–H), 3.00 (ddd, 4.9, 4.6, 2.8 Hz, C5–H), 4.17 (dd, 4.9, 1.5 Hz, C4–H), 5.23 (dd, 5.5, 2.8 Hz, C6–H), 6.29 (dd, 5.5, 2.8 Hz, C7–H), 6.63 (dd, 6.7, 1.5 Hz, C2–H), 6.8–7.2 (m, Ph). ^{13}C NMR ($CDCl_3$, r.t.): 39.3, 45.7, 46.8 (C1, C4, C5), 43.4 (C8), 130.0, 132.7, 139.9 (C2, C6, C7), 125.6, 125.9, 126.2, 127.7, 127.9, 128.6 (C_o, C_m, C_p), 136.9, 140.9, 141.3 (C_{ipso}, C3). UV–Vis (Et_2O): λ_{max} (nm) (lg ϵ): 208 (1.738), 258 (1.441). MS *m/z* [%]: 258 [79, M^+], 217 [38], 167 [100, $M^+ - C_7H_7$].

(4) Pentacarbonyl{6,7-η²-[3-endo-4-diphenyl-8-oxa-bicyclo[3.2.1]octa-2,6-diene]}tungsten (9a)

5 ml of furan (**8a**) were added to the solution of **4** (see (1)). Within 14 h at −30 °C the colour of the solution changed to red–brown. The solvent and excess **8a** were removed *in vacuo*. The residue was redissolved in pentane and chromatographed on silica gel using pentane/CH_2Cl_2 (3:1) as the eluant. The light orange band was eluted and the solvent removed *in vacuo* at −30 °C to give a yellow powder. Yield 1.2 g (58% based on **1**). M.p. 147 °C (dec.).

IR (n-pentane): ν(CO) 2083m, 1967vs, 1952s cm^{-1}. ^{1}H NMR ($CDCl_3$, r.t.): 3.93 (d, 5.5 Hz, C6–H), 4.57 (dd, 5.5, 1.8 Hz, C4–H), 4.84 (d, 4.9 Hz, C1–H), 5.04 (d, 5.5 Hz, C5–H), 5.08 (d, 5.5 Hz, C7–H), 6.67 (dd, 4.9, 1.8 Hz, C2–H), 7.0–7.3 (m, Ph). ^{13}C NMR ($CDCl_3$, −45 °C): 45.5 (C4), 68.7, 80.3, 82.3 (C1, C5, C6, C7), 125.7, 126.8, 127.4, 127.8, 128.2, 128.6 (C_o, C_m, C_p, C2), 135.1, 137.6, 138.4 (C_{ipso}, C3), 195.8 (*cis*-CO), 201.0 (*trans*-CO). MS *m/z* [%]: 584 [2, M^+], 444 [1, $M^+ - 5CO$], 260 [100, $M^+ - W(CO)_5$]. *Anal.* Calc. for $C_{24}H_{16}O_6W$: C, 49.34; H, 2.76. Found: C, 48.95; H, 3.14%.

(5) Pentacarbonyl{6,7-η²-[3-endo-4-diphenyl-5-methyl-8-oxa-bicyclo[3.2.1]octa-2,6-diene]}tungsten (9b)

5 ml of 2-methylfuran (**8b**) were added to the solution of **4** (see (1)). Reaction time: 16 h at −30 °C. For the purification of the complex see (3). Orange crystals. Yield 1.1 g (51% based on **1**). M.p. 128 °C (dec.).

IR (n-pentane): ν(CO) 2083m, 1967vs, 1952s cm^{-1}. ^{1}H NMR ($CDCl_3$, −30 °C): 1.81 (s, CH_3), 4.25 (d, 5.5 Hz, C6–H), 4.31 (d, 1.8 Hz, C4–H), 4.90 (d, 4.9 Hz, C1–H), 5.16 (d, 5.5 Hz, C7–H), 6.68 (dd, 4.9, 1.8 Hz, C2–H), 7.1–7.3 (m, Ph). ^{13}C NMR ($CDCl_3$, −30 °C): 26.6 (C8), 51.9 (C4), 79.2, 85.7 (C1, C5, C6, C7), 126.1, 126.8, 127.1, 127.3, 128.1, 128.2 (C_o, C_m, C_p, C2), 135.2, 138.8, 140.2 (C_{ipso}, C3), 196.0 (*cis*-CO), 200.7 (*trans*-CO). MS *m/z* [%]: 598 [1, M^+], 458 [5, $M^+ - 5CO$], 274 [56, $M^+ - W(CO)_5$], 231 [100]. *Anal.* Calc. for $C_{25}H_{18}O_6W$: C, 50.19; H, 3.03. Found: C, 50.26; H, 3.33%.

(6) Pentacarbonyl{6,7-η²-[3-endo-4-diphenyl-7-methyl-8-oxa-bicyclo[3.2.1]octa-2,6-diene]}tungsten (9c)

2.5 ml of 3-methylfuran (**8c**) were added to the solution of **4** (see (1)). Reaction time: 22 h at -30 °C. For the purification of the complex see (3). Orange crystals. Yield 970 mg (51% based on **1**). M.p. 98 °C (dec.).

IR (n-pentane): ν(CO) 2079m, 1961vs, 1944s, cm^{-1}. ^{1}H NMR ($CDCl_3$, −30 °C): 2.57 (s, CH_3), 4.00 (s, C6–H), 4.58 (dd, 5.6, 1.8 Hz, C4–H), 4.92 (d, 4.6 Hz, C1–H), 5.00 (d, 5.6 Hz, C5–H), 7.0–7.3 (m, Ph). ^{13}C NMR ($CDCl_3$, −40 °C): 21.0 (C8), 45.6 (C4), 79.2 (C5), 83.4 (C1, C6), 125.6, 126.8, 127.4, 128.2, 128.3, 128.5, 128.7 (C_o, C_m, C_p, C2), 135.3, 137.6, 138.3 (C_{ipso}, C3), 196.8 (*cis*-CO), 201.1 (*trans*-CO). MS *m/z* [%]: 598 [1, M^+], 458 [2, $M^+ - 5CO$], 274 [63, $M^+ - W(CO)_5$], 245 [100]. *Anal.* Calc. for $C_{25}H_{18}O_6W$: C, 50.19; H, 3.03. Found: C, 49.88; H, 3.16%.

(7) 3-endo-4-Diphenyl-8-oxa-bicyclo[3.2.1]octa-2,6-diene (10a)

A solution of 230 mg (0.4 mmol) (**9a**) and 7.5 g NEt_4Br in 20 ml of dichloromethane was stirred for

12 h at room temperature. The solvent was removed *in vacuo* and the residue was extracted three times with 25 ml of Et_2O each. The solvent was removed *in vacuo* and the yellow oily residue was purified by thin layer chromatography (eluant: pentane/CH_2Cl_2 1:1; R_f of **10a**: 0.31). Colourless crystals. Yield 72 mg (70%). M.p. 62 °C.

^{1}H NMR ($CDCl_3$, r.t.): 4.46 (dd, 5.8, 1.5 Hz, C4–H), 4.88 (dd, 4.9, 1.7 Hz, C1–H), 5.08 (dd, 5.8, 1.8 Hz, C5–H), 5.48 (dd, 6.1, 1.8 Hz, C6–H), 6.57 (dd, 6.1, 1.7 Hz, C7–H), 6.62 (dd, 4.9, 1.5 Hz, C2–H), 6.9–7.2 (m, Ph). ^{13}C NMR ($CDCl_3$, r.t.): 44.9 (C4), 76.4 (C5), 82.5 (C1), 126.0, 126.4, 127.0, 127.5, 128.0, 128.2, 128.7, 129.0 (C_o, C_m, C_p, C2, C6) 138.9 (C7), 136.2, 137.1, 139.6 (C_{ipso}, C3). UV–Vis (Et_2O): λ_{max} (nm) (lg ϵ): 208 (1.728), 258 (1.379). MS *m/z* [%]: 260 [100, M^+], 231 [87].

*(8) 3-endo-4-Diphenyl-5-methyl-8-oxa-bicyclo-[3.2.1]octa-2,6-diene (**10b**)*

A solution of 280 mg (0.4 mmol) (**9b**) and 8.5 g NEt_4Br in 20 ml of dichloromethane was stirred for 20 h at room temperature. For the purification of the compound see (7) (eluant: pentane/CH_2Cl_2 1:1; R_f of **10b**: 0.41). Colourless crystals. Yield: 58 mg (45%). M.p. 64 °C.

^{1}H NMR ($CDCl_3$, −30 °C): 1.55 (s, CH_3), 4.14 (d, 1.8 Hz, C4–H), 4.99 (dd, 4.9, 1.7 Hz, C1–H), 5.49 (d, 5.8 Hz, C6–H), 6.57 (dd, 5.8, 1.7 Hz, C7–H), 6.68 (dd, 4.9, 1.8 Hz, C2–H), 7.0–7.2 (m, Ph). ^{13}C NMR ($CDCl_3$, r.t.): 23.0 (CH_3), 52.1 (C4), 68.2 (C5), 86.5 (C1), 126.3, 126.4, 126.7, 127.8, 127.9, 128.6, 128.8, 129.9 (C_o, C_m, C_p, C2, C6), 136.8 (C7), 136.3, 139.3, 139.8 (C_{ipso}, C3). UV–Vis (Et_2O): λ_{max} (nm) (lg ϵ): 208 (1.759), 256 (1.476). MS *m/z* [%]: 274 [43, M^+], 231 [100], 95 [39], 91 [21].

*(9) 3-endo-4-Diphenyl-7-methyl-8-oxa-bicyclo[3.2.1]-octa-2,6-diene (**10c**)*

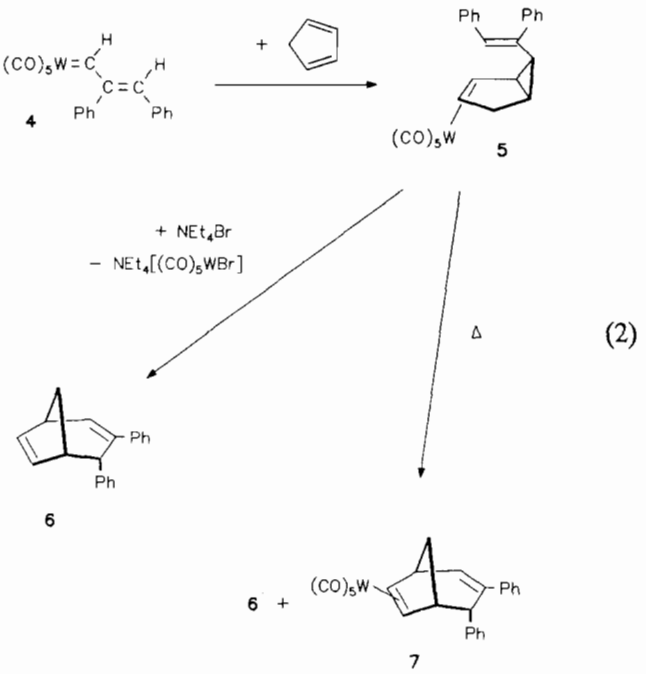
A solution of 420 mg (0.4 mmol) (**9c**) and 7 g NEt_4Br in 20 ml of dichloromethane was stirred for 15 h at room temperature. For the purification of the compound see (7) (eluant: pentane/CH_2Cl_2 3:2; R_f of **10c**: 0.28). Colourless crystals. Yield: 68 mg (39%). M.p. 68 °C.

^{1}H NMR ($CDCl_3$, −30 °C): 1.97 (s, CH_3), 4.49 (dd, 5.8, 1.8 Hz, C4–H), 4.68 (d, 4.7 Hz, C1–H), 5.05 (dd, 5.8, 1.7 Hz, C5–H), 5.12 (q, 1.7 Hz, C6–H), 6.79 (dd, 4.7, 1.8 Hz, C2–H), 6.9–7.2 (m, Ph). ^{13}C NMR ($CDCl_3$ r.t.): 13.0 (CH_3), 45.2 (C4), 79.4 (C5), 83.2 (C1), 121.1, 126.0, 126.3, 126.9, 128.0, 128.1, 128.6, 129.0 (C_o, C_m, C_p, C2, C6), 136.9, 137.9, 139.8 (C_{ipso}, C3), 149.9 (C7). UV–Vis (Et_2O): λ_{max} (nm) (lg ϵ): 208 (1.833), 258 (1.535). MZ *m/z* [%]: 274 [82, M^+], 245 [100], 95 [94].

Results and discussion

*Reaction of **4** with cyclopentadiene*

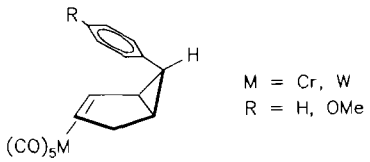
The allylidene complex **4**, generated *in situ* following the sequence **1**→**2**→**3**→**4** of eqn. (1), reacts in dichloromethane at −30 °C with cyclopentadiene in excess (10 to 20 fold) slowly to give the η^2-*cis*-divinylcyclopropane complex **5** (eqn. (2)). The reaction is almost quantitative and proceeds chemo- and stereoselectively. According to the NMR spectra only one isomer is formed. Isolated pure **5** is obtained from **1** in an overall yield of *c.* 54%.



(2)

As a solid **5** is stable in air and at room temperature; solutions of **5** in CH_2Cl_2 or other polar solvents decompose within *c.* 30 to 90 min. The IR spectrum of **5** indicates that the pentacarbonyl fragment of **4** remains intact on reaction with cyclopentadiene. The ^{1}H NMR spectrum shows in the low-field region ($\delta > 4$ ppm) three signals for olefinic protons in addition to resonances for 10 aromatic protons. Two of these olefinic resonances are at rather high field ($\delta = 4.40$ and 4.66) characteristic of coordinated olefins. There is no low-field signal with $\delta > 7.5$. Therefore the structure of a Diels–Alder adduct (see **C** in Scheme 1) can be excluded. For such a complex of low-field resonance at $\delta \approx 15$ due to the W=C unit only two olefinic signals would be expected. The high-field (ring) resonances ($\delta < 4$ ppm) are similar to those of the previously synthesized *cis*-vinylcyclopropane complexes **D** [13]. The similarity supports the structural proposal shown in eqn. (2). The structure of **D** was established by spectroscopic means and additionally for M = Cr and R = OMe by an X-ray

diffraction study. To our knowledge **5** is the first isolated *cis*-divinylcyclopropane complex. η^2- and η^4-*cis*-divinylcyclopropane complexes of a related type have been described for Mo, Fe and Rh [14].



D

In dichloromethane at room temperature **5** reacts slowly with bromides to give $[(CO)_5WBr]^-$ and an organic product (**6**) (eqn. (2)). According to the NMR and mass spectra compound **6** is not the free ligand of **5** but rather an isomer of the *cis*-divinylcyclopropane. The structural assignment of **6** is based on its ^1H and ^{13}C NMR spectra, homo-decoupling experiments, and the similarity of its spectra with those of related compounds [15]. The coupling constant J((C4–H)–(C5–H)) of 4.5 Hz indicates the *endo* isomer. The *cis*-divinylcyclopropane and the *exo* isomer of **6** have not been detected.

Compound **6** is also formed when solutions of **5** in dichloromethane are kept at −30 °C for several days. In addition to **6** its pentacarbonyl complex **7** can be detected in solution. Complex **7** has not been isolated but has only been identified by its ^1H NMR and IR spectra. From the large high-field shift of C6–H and C7–H (see Fig. 2) on complexation it follows that **6** is coordinated to the metal via C6–C7. The *exo* position of the $(CO)_5W$ fragment can be deduced from the decrease of the coupling constants J((C1–H)–(C7–H)) and J(C5–H)–(C6–H)) and the high-field shift of the CH_2 protons on complexation.

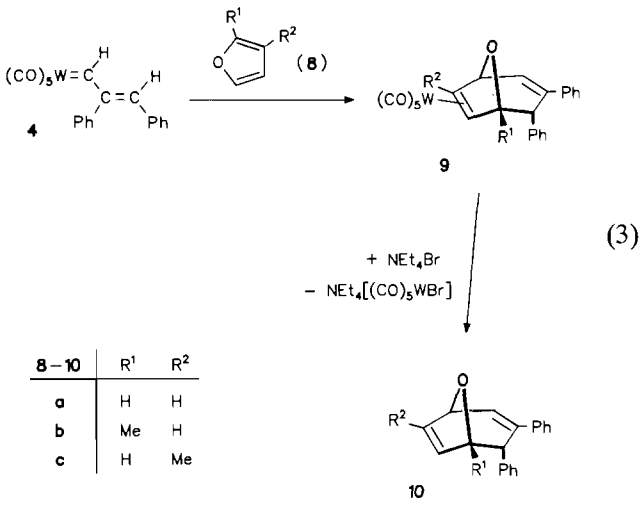
The two most likely mechanisms to account for the formation of **6** from **5** are (i) decomplexation of the *cis*-divinylcyclopropane followed by Cope rearrangement to give **6** or (ii) metal-centred rearrangement **5**→**7** followed by decoordination of **6**. The time dependent ^1H NMR spectra of a mixture of **5**/PMe_3 in $CDCl_3$ at −40 °C only show the gradual decrease of the intensity of the resonances of **5** and PMe_3 and an increase of those of **6** and $(CO)_5W[PMe_3]$. Signals due to **7** or any intermediate cannot be detected. Since it is well known that *cis*-divinylcyclopropanes usually undergo fast Cope rearrangement at or even below room temperature path (i) seems more likely. However, path (ii) cannot be completely ruled out. Complex **7** is probably formed from **6** and a solvent-stabilized $(CO)_5W$ fragment produced by decomplexation of the divinylcyclopropane.

Recently, *cis*-divinylcyclopropanes were obtained in the $Rh_2(OAc)_4$-catalyzed reaction of cyclopentadiene with dienes EtOOC–C(N_2)–CH=C(X)COOEt [16] in which a rhodium carbene complex may act as an intermediate. The divinylcyclopropanes are isolable only in cases where the substituent X is non-hydrogen and can be converted by a mild thermolysis to the corresponding Cope rearrangement products.

The reaction of **4** with cyclopentadiene is chemospecific. The formation of Diels–Alder adducts (**C** in Scheme 1) has not been observed. In contrast to **4** the heteroatom-stabilized carbene complex $(CO)_5W$=C(CH=CH_2)OMe reacts with cyclopentadiene by [4+2] cycloaddition [17]. An exchange of OMe for H in $(CO)_5W$=C(CR=CR_2)OMe increases the electrophilicity of the carbene carbon and simultaneously activates the C=C bond toward [4+2] cycloaddition. The cyclopropanation of olefins with strongly electrophilic carbene complexes such as **2** and **4** is initiated by a nucleophilic attack of the olefin at the carbene carbon [11a, 18]. Therefore our results show that obviously the activation of the carbene carbon through OMe/H exchange overcompensates that of the dienophilic C=C bond.

Reactions of 4 with furans

Complex **4** reacts with furan (**8a**) slightly faster than with cyclopentadiene. The relative reactivity as determined by competition experiments is 1.17±0.05. From the reaction mixture complex **9a** is isolated in *c.* 58% yield (eqn. (3)). The analogous reaction of **4** with 2- and 3-methylfuran affords the complexes **9b** and **9c**, respectively. All reactions are chemo-, regio- and stereoselective. The formation of only one isomer was observed; intermediates could not be detected. The relative reactivities are cyclopentadiene: **8a**:**8b**:**8c** = 1:1.17(5):12.3(2):53(4).



At room temperature in solution the complexes are labile and decompose by decomplexation of the bicyclic ligands **10a–c** (eqn. (3)) and formation of $W(CO)_6$. The stability of **9c** is significantly lower than that of

9a or **9b**. Generally addition of NEt_4Br enhances the rate of decoordination.

The structures of **9** and **10** have been established by their ^1H NMR spectra and by homo-decoupling experiments. The bicyclic ligands coordinate to the $(CO)_5W$ fragment via the C6–C7 double bond (the unsubstituted C=C in **9a** and **9b**). This follows from the low-field shift of at least 0.8 ppm of C6–H and C7–H on decomplexation. The coupling constants J((C4–H)–(C5–H)) of 5.5–5.8 Hz in **9a,c** and **10a,c** together with the allylic coupling constants J((C2–H)–(C4–H)) of 1.5–1.8 Hz in **9** and **10** establish the *endo* arrangement of the phenyl group (see eqn.(3)). On decoordination the values for the coupling constants J((C5–H)–(C6–H)) and J((C1–H)–(C7–H)) increases significantly. In **9** the coupling cannot be resolved any more by the spectrometer used (250 MHz); in **10** ^3J is 1.5 Hz. This indicates that on decoordination the dihedral angles H–C1–C7–H and H–C5–C6–H decrease. Therefore the $(CO)_5W$ fragment occupies the *exo* position thus avoiding steric interaction with the C4 phenyl group.

In **9a,c** and **10a,c** the signal of C4–H appears as a doublet of a doublet (^3J=5.8 Hz, ^4J=1.5 and 1.8 Hz, respectively); in **9b** and **10b** it is only a doublet (^4J=1.8 Hz). Therefore the methyl substituent in **9b** and **10b** is bonded to the bridge-head carbon C5. In **9c/10c** the methyl group is connected to the olefinic carbon C7 as can be deduced from the absence of the $^3J(cis)$ coupling.

Although an intermediate has not been detected it is reasonable to assume that the reaction of **4** with **8** proceeds analogously to that of **4** with cyclopentadiene. The first reaction step involves regio- and stereospecific formation of a divinylcyclopropane complex. The transfer of the carbene ligand of **4** to the unsubstituted double bond of 2-methylfuran (**8b**) and to the substituted double bond of 3-methylfuran (**8c**) follows from the stereochemistry of the isolated products. The initial reaction step in the cyclopropanation reaction is a nucleophilic attack of the olefin at the metal coordinated carbene carbon atom [11a, 18]. Therefore, if there is a choice, an attack of the most nucleophilic C atom of **8** (C5 of **8b** [19] and C2 of **8c**, see Fig. 3) at the carbene carbon of **4** is to be expected. This is in line with the stereochemistry of the proposed divinylcyclopropane complexes.

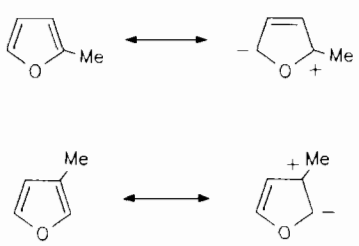


Fig. 3. Resonance structures of **8b** and **8c**.

The subsequent reaction steps probably involve decomplexation of divinylcyclopropane, Cope rearrangement and recoordination of **10**. Generally $(CO)_5W$(vinylether) complexes are significantly less stable than $(CO)_5W$(olefin) complexes which could explain why **4** can be isolated whereas the corresponding divinylcyclopropane complexes from **4** and **8** rapidly isomerize to form **9**. The high rate of the Cope rearrangement requires a *cis*-arrangement of the vinyl groups.

Since the rate-limiting reaction step very likely is the formation of the divinylcyclopropane complex it is interesting to compare the relative reactivity of cyclopentadiene and **8** towards **4** with that of olefins and vinylethers towards **2** [11a, 20]. The relative reactivity of propene, ethyl vinyl ether and 2-methoxypropene towards **2** is 1:1550:34500. Although the same trend is observed in the reaction rate of **4** with cyclopentadiene, in **8a**, **8b** and **8c** the increase in the reaction rate is much less pronounced, probably due to the aromaticity of the substrates **8**.

The results demonstrate that non-heteroatom-stabilized allylidene complexes can be employed in formal [4+3] cycloadditions via tandem cyclopropanation/Cope rearrangement to produce seven-membered ring systems. The reactions are fast and proceed in a highly regio- and stereoselective way.

Acknowledgements

Support of this work by the Volkwagen-Stiftung, the Fonds der Chemischen Industrie and the Government of Baden-Württemberg (Schwerpunkt 'Metallzentrierte Substrattransformationen') is gratefully acknowledged.

References

1 K.H. Dötz, *Angew. Chem., 87* (1975) 672; *Angew. Chem., Int. Ed. Engl., 14* (1975) 644.

2 (a) K.H. Dötz, in K.H. Dötz, H. Fischer, P. Hofmann, F.R. Kreissl, U. Schubert and K. Weiss (eds.), *Transition Metal Carbene Complexes,* Verlag Chemie, Weinheim, 1983, p. 191; (b) K.H. Dötz, *Angew. Chem., 96* (1984) 573; *Angew. Chem., Int. Ed. Engl., 23* (1984) 587.

3 (a) T.J. Katz and J.S. Lee, *J. Am. Chem. Soc., 102* (1980) 422; (b) T. Masuda and T. Higashimura, *Adv. Polym. Sci., 81* (1986) 121; (c) J. Feldman and R.R. Schrock, *Prog. Inorg. Chem., 39* (1991) 1.

4 (a) P. Hofmann and M. Hämmerle, *Angew. Chem., 101* (1989) 101; *Angew. Chem., Int. Ed. Engl., 28* (1989) 908; (b) P. Hofmann, M. Hämmerle and G. Unfried, *New. J. Chem., 15* (1991) 769.

5 (a) W.D. Wulff, D.C. Young and C.K. Murray, *Pure Appl. Chem., 60* (1988) 137; (b) A. Wienand and H.-U. Reissig, *Chem. Ber., 124* (1991) 957.

6 (a) W.D. Wulff, D.C. Young and C.K. Murray, *J. Am. Chem. Soc., 110* (1988) 2653; (b) W.D. Wulff, W.E. Bauta, R.W. Kaesler, P.J. Lankford, R.A. Miller, C.K. Murray and D.C. Young, *J. Am. Chem. Soc., 112* (1990) 3642.

7 G.-H. Kuo. P. Helquist and R.C. Kerber, *Organometallics, 3* (1984) 806.

8 (a) C.P. Casey and W.H. Miles, *Organometallics, 3* (1984) 808; (b) C.P. Casey, W.H. Miles and H. Tukada, *J. Am. Chem. Soc., 107* (1985) 2924; (c) R.U. Vargas, R.D. Theys and M.M. Hossain, *J. Am. Chem. Soc., 114* (1992) 777.

9 H. Fischer, J. Hofmann and E. Mauz, *Angew. Chem., 103* (1991) 1013; *Angew. Chem., Int. Ed. Engl., 30* (1991) 998.

10 C.P. Casey, S.W. Polichnowski, H.E. Tuinstra, L.D. Albin and J.C. Calabrese, *Inorg. Chem., 17* (1978) 3045.

11 (a) C.P. Casey, S.W. Polichnowski, A.J. Shusterman and C.R. Jones, *J. Am. Chem. Soc., 101* (1979) 7282; (b) H. Fischer, S. Zeuner and K. Ackermann, *J. Chem. Soc., Chem. Commun.,* (1984) 684.

12 D.M. Burness, in N. Rabjahn (ed.), *Organic Synthesis,* Coll. Vol. IV, Wiley, New York, 1963, p. 649.

13 H. Fischer and J. Hofmann, *Chem. Ber., 124* (1991) 981.

14 (a) R. Aumann, *Angew. Chem., 82* (1970) 810; *Angew. Chem., Int. Ed. Engl., 9* (1970) 800; (b) *J. Organomet. Chem., 66* (1974) C6; (c) *77* (1974) C33; (d) R. Aumann and M. Runge, *Chem. Ber., 125* (1992) 259.

15 (a) M. Christl and D. Brückner, *Chem. Ber., 119* (1989) 2025; (b) G.B. Trimitsis and B. Zimmermann, *J. Chem. Soc., Chem. Commun.,* (1984) 1506.

16 H.M.L. Davies, H.D. Smith and O. Korkor, *Tetrahedron Lett.,* (1987) 1853.

17 W.D. Wulff and D.C. Young, *J. Am. Chem. Soc., 105* (1983) 6726.

18 H. Fischer, E. Mauz, M. Jaeger and R. Fischer, *J. Organomet. Chem., 427* (1992) 63.

19 P.V. Alston and R.M. Ottenbrite, *J. Org. Chem., 40* (1975) 1111.

20 M.P. Doyle, J.H. Griffin, V. Bagheri and R.L. Dorow, *Organometallics, 3* (1984) 53.