Manganese and tungsten carbene complex mediated intramolecular Diels–Alder reactions*

K.H. Dötz**, D. Böttcher and M. Jendro

Institut für Organische Chemie und Biochemie, Rheinische Friedrich-Wilhelms-Universität, Gerhard-Domagk-Straße 1, D-53121 Bonn (Germany) and Fachbereich Chemie der Philipps-Universität, Hans-Meerwein-Straße, D-35043 Marburg (Germany)

(Received March 1, 1994)

Abstract

Diene-dienophile-functionalized Fischer-type carbene complexes containing 2-furfurylamino(2-propenyl)carbene ligands have been prepared from hexacarbonyl tungsten and tricarbonyl(methylcyclopentadienyl)manganese. These complexes are distinctly more reactive towards intramolecular Diels–Alder reactions than their acrylic amide congeners. Their reactivity increases with the electron acceptor capacity of the coligand metal fragment and with increasing steric bulk of the amino group.

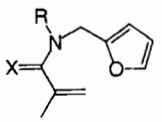
Key words: Diels–Alder reactions; Manganese complexes; Tungsten complexes; Carbene complexes

Introduction

During the past two decades Fischer-type carbene complexes $(CO)_5M{=}C(R)R'$ have received increasing attention as useful reagents in organic synthesis. This type of compound is characterized by an electrophilic carbene carbon atom attached to a low-valent metal center [2]. Their synthetic scope aims both at carbene ligand centered carbon carbon bond formation and at metal-induced interligand coupling processes [3–5]. The latter type of reaction is based on the bifunctionality of carbonyl carbene complexes exploited in template reactions such as the thermal chromium-mediated carbene annulation by alkynes [6] or the photochemically induced generation of ketene intermediates which can be trapped subsequently in cycloaddition reactions or by addition of protic nucleophiles [4].

The intrinsic α-CH acidity of alkyl carbene ligands was early recognized [7] and has been recently exploited in stereoselective aldol and Michael reactions [8, 9]. According to the isolobal analogy of an $M(CO)_5$ fragment (M = Cr, Mo, W) and an oxygen atom Fischer-type complexes can be regarded as metal-tuned carbonyl compounds [10]. Along these lines alkoxy and amino-carbene complexes are organometallic analogues of esters and carboxylic amides. As such vinyl and ethynyl carbene ligands have been found to be potent dienophiles in [4 + 2] cycloaddition reactions [11]. In general, metal carbene based Diels–Alder reactions occur under mild conditions with excellent stereoselectivities which, at room temperature, may exceed those obtained at −78 °C under Lewis acid catalysis. These results suggest that the pentacarbonyl metal fragment represents a potent electrophile even superior to a Lewis acid coordinated oxygen atom.

Recently, we have focussed on the intramolecular version of the Diels–Alder reaction [12] which has been established as a powerful tool for stereoselective carbon carbon bond formation [13]. Here we report a comparative study based on manganese and tungsten complexes (Scheme 1).



1 - 9

R	X = $(CO)_5W$	$MeCp(CO)_2Mn$	O
H	**1**	**4**	**7**
CH_3	**2**	**5**	**8**
$CH_2C_6H_5$	**3**	**6**	**9**

Scheme 1.

*Reactions of Complex Ligands, Part 59. For Part 58 see ref. 1.

**Author to whom correspondence should be addressed.

SSDI 0020-1693(94)03920-J

Experimental

All reactions were carried out in Schlenk tubes under an atmosphere of dry nitrogen. Solvents were dried using standard methods, distilled, saturated and stored under nitrogen. The silica gel used for chromatography (type 60, E. Merck, Darmstadt, 0.063–0.2 mm) was dried at high vacuum and kept under nitrogen. The following instruments served for spectroscopic characterization: IR spectrometer: Nicolet 510; NMR spectrometer: Bruker AC 300 or Bruker AMX 500; mass spectrometer: Varian MAT 311 A and Varian MAT CH7 A. Elemental analysis was carried out on a Heraeus CHN rapid element analyzer.

The preparation and characterization of the tungsten carbene complex **10** occurred as described in the literature [12].

Preparation of pentacarbonyl[(E)-N-2-furfurylamino-(2-propenyl)carbene]tungsten (1)

A solution of 0.35 ml (4.00 mmol) 2-furfurylamine in 5 ml of dichloromethane was added slowly at −78 °C to a solution of 0.82 g (2.00 mmol) pentacarbonyl[methoxy(2-propenyl)carbene]tungsten [12] in 10 ml dichloromethane. After stirring for 1/2 h the reaction mixture was allowed to warm to room temperature. Removal of the solvent was followed by purification by chromatography over silica gel in petroleum ether/dichloromethane (3/1) to give 0.82 g (87%) **1** as a yellow solid. *Anal.* Calc. for $C_{14}H_{11}NO_6W$ (473.10): C, 35.54; H, 2.34; N, 2.96. Found: C, 35.52; H, 2.32; N, 2.85%. IR (ν(CO), petroleum ether): 2066 (m), 1971 (w), 1942 (vs), 1921 (s) cm^{-1}. ^1H NMR (300 MHz, acetone-d^6): $\delta = 10.77$ (s, 1H, NH), 7.58 (dd, $J = 0.97$, 1.88 Hz, 1H, furyl-H(5)), 6.45 (dd, $J = 1.96$ Hz, 1H, furyl-H(4)), 6.41 (dd, $J = 0.70$, 3.29 Hz, 1H, furyl-H(3)), 4.78 (q, $J = 1.36$ Hz, 1H, =CH(*Z*)), 4.76 (d, $J = 5.92$ Hz, 2H, CH_2), 4.52 (q, $J = 0.81$ Hz, 1H, =CH(*E*)), 1.99 (dd, $J = 0.92$, 1.45 Hz, 3H, CH_3) ppm. ^{13}C NMR (126 MHz, acetone-d^6): $\delta = 256.7$ (d, $J = 80.28$ Hz, carbene-C), 204.0 (d, $J = 128.87$ Hz, *trans*-CO), 199.2 (d, $J = 127.24$ Hz, *cis*-CO), 153.6 (furyl-C(2)), 149.1 (=C(2)), 143.9 (furyl-C(5)), 111.4 (furyl-C(3)), 109.9 (furyl-C(4)), 104.7 (=C(1)), 46.6 (CH_2), 19.9 (CH_3) ppm.

Preparation of pentacarbonyl[(E)-N-2-furfuryl-N-methylamino-(2-propenyl)carbene]tungsten (2)

0.053 g (2.20 mmol) sodium hydride was added to a solution of 0.95 g (2.00 mmol) **1** in 20 ml tetrahydrofuran at 0 °C. After stirring for 30 min 0.14 ml (2.20 mmol) methyl iodide was added dropwise. The solution was brought to room temperature and stirred for 1 h. The solvent was removed at reduced pressure and the residue was purified by chromatography over silica gel in petroleum ether/dichloromethane 3/1 to give 0.877 g (90%) **2** as yellow crystals. *Anal.* Calc. for $C_{15}H_{13}NO_6W$ (487.12): C, 36.98; H, 2.69; N, 2.88. Found: C, 37.22; H, 2.72; N, 2.83%. IR (ν(CO), petroleum ether): 2064 (m), 1971 (w), 1942 (vs) cm^{-1}. ^1H NMR (300 MHz, acetone-d^6): $\delta = 7.61$ (dd, $J = 0.74$, 1.85 Hz, 1H, furyl-H(5)), 6.54 (dd, $J = 1.94$, 3.27 Hz, 1H, furyl-H(4)), 6.47 (dd, $J = 0.71$, 3.25 Hz, 1H, furyl-H(3)), 5.06, 5.03 (2d, $J = 14.90$ Hz, 2H, CH_2), 4.76 (q, $J = 1.26$ Hz, 1H, =CH(*Z*)), 4.54 (q, $J = 0.79$ Hz, =CH(*E*)), 3.73 (s, 3H, NCH_3), 2.00 (dd, $J = 0.95$, 1.47 Hz, 3H, =C(CH_3)) ppm. ^{13}C NMR (75 MHz, acetone-d^6): $\delta = 257.9$ (carbene-C), 204.0 (*trans*-CO), 199.6 (d, $J = 127.32$ Hz, *cis*-CO), 155.8 (furyl-C(2)), 148.7 (=C(2)), 144.6 (furyl-C(5)), 111.6 (furyl-C(3)), 111.5 (furyl-C(4)), 105.7 (=C(1)), 52.6 (NCH_3), 51.0 (CH_2), 20.6 (=C(CH_3)) ppm.

Preparation of pentacarbonyl[(E)-N-benzyl-N-2-furfurylamino-(2-propenyl)carbene]tungsten (3)

As described for **2**, complex **3** was obtained from 0.95 g (2.00 mmol) **1**, 0.053 g (2.20 mmol) sodium hydride and 0.26 ml (2.20 mmol) benzyl bromide as yellow crystals (0.71 g; 63%). *Anal.* Calc. for $C_{21}H_{17}NO_6W$ (563.22): C, 44.78; H, 3.04; N, 2.46. Found: C, 44.78; H, 2.98; N, 2.33%. IR (ν(CO), petroleum ether): 2064 (m), 1971 (w), 1937 (vs) cm^{-1}. ^1H NMR (300 MHz, acetone-d^6): $\delta = 7.63$ (dd, $J = 0.73$, 1.83 Hz, 1H, furyl-H(5)), 7.44 (m, 5H, phenyl-H), 6.47 (dd, $J = 1.86$, 3.29 Hz, 1H, furyl-H(4)), 6.42 (dd, $J = 0.54$, 3.04 Hz, 1H, furyl-H(3)), 5.16, 5.01 (2d, $J = 15.40$ Hz, 2H, phenyl-CH_2), 4.93, 4.84 (2d, $J = 15.11$ Hz, 2H, furyl-CH_2), 4.86 (s, 1H, =CH(*Z*)), 4.70 (s, 1H, =CH(*E*)), 2.13 (s, 3H, =C(CH_3)) ppm. ^{13}C NMR (75 MHz, acetone-d^6): $\delta = 262.1$ (carbene-C), 203.6 (*trans*-CO), 199.2 (*cis*-CO), 155.8 (furyl-C(2)), 148.1 (=C(2)), 144.6 (furyl-C(5)), 134.9 (phenyl-C(1)), 129.9 (phenyl-C(3, 5)), 129.1 (phenyl-C(2, 6)), 128.0 (phenyl-C(4)), 111.7 (furyl-C(3)), 111.6 (furyl-C(4)), 106.1 (=C(1)), 65.6 (phenyl-CH_2), 49.3 (furyl-CH_2), 20.6 (=C(CH_3)) ppm.

Preparation of dicarbonyl[(E,Z)-N-2-furfurylamino-(2-propenyl)carbene](methylcyclopentadienyl)manganese (4)

At −78 °C 0.89 ml (10 mmol) 2-bromopropene was added dropwise to a solution of 11.8 ml (20 mmol) 1.7 M tert-butyllithium in 50 ml diethyl ether. The mixture was stirred for 3 h and then added slowly at −30 °C to a solution of 1.58 ml (10 mmol) tricarbonyl(methylcyclopentadienyl)manganese and 1.50 ml (10 mmol) tetramethylethylenediamine (TMEDA) in 50 ml diethyl ether. After 1 h the solution was warmed to room temperature. Removal of the solvent gave the lithium acylmetallate as a brownish solid. The crude intermediate was dissolved in dichloromethane at −40 °C and 1.05 ml (7 mmol) TMEDA were added. After adding successively 0.74 ml (10 mmol) acetylbromide

and 0.88 ml (10 mmol) 2-furfurylamine the solution was stirred overnight.

Removal of the solvent at reduced pressure and chromatography on silica gel using petroleum ether/diethyl ether (8/1) at −10 °C gave 1.19 g (35%) of a red–brown oil as a mixture of *E/Z*-isomers in a 3:1 ratio. *Anal.* Calc. for $C_{17}H_{18}MnNO_3$ (339.27): C, 60.18; H, 5.35; N, 4.13. Found: C, 60.53; H, 5.61; N, 4.16%. IR (ν(CO), petroleum ether): 1928 (s), 1873 (s) cm^{-1}. ^1H NMR (300 MHz, acetone-d^6): δ=9.54 (s, 1H, NH, *E*-isomer), 9.35 (s, 1H, NH, *Z*-isomer), 7.55 (s, 1H, furyl-H(5)), 6.34–6.44 (m, 2H, furyl-H(3, 4)), 5.16 (s, 2H, NCH_2, *Z*-isomer), 4.28–4.65 (m, 8H, cyclopentadienyl-H-2–5, $=CH_2$, NCH_2, *E*-isomer), 1.99 (s, 3H, cyclopentadienyl-CH_3, *E*-isomer), 1.94 (s, 3H, cyclopentadienyl-CH_3, *Z*-isomer), 1.90 (s, 3H, $=C(CH_3)$) ppm. ^{13}C NMR (75 MHz, acetone-d^6): *E*-isomer: δ=288.2 (carbene-C), 235.0 (CO), 160.3 (furyl-C(2)), 151.8 (=C(2)), 143.4 (furyl-C(5)), 111.5 (furyl-C(3)), 108.6 (furyl-C(4)), 103.6 (=C(1)), 101.5 (cyclopentadienyl-C-1), 85.5 (cyclopentadienyl-C(2, 5)), 84.0 (cyclopentadienyl-C(3, 4)), 46.3 (NCH_2), 22.0 ($=C(CH_3)$), 14.2 (cyclopentadienyl-CH_3) ppm; *Z*-isomer: δ=286.4 (carbene-C), 235.0 (CO), 160.3 (furyl-C(2)), 151.4 (=C(2)), 143.6 (furyl-C(5)), 111.5 (furyl-C(3)), 109.3 (furyl-C(4)), 103.3 (=C(1)), 100.7 (cyclopentadienyl-C(1)), 85.3 (cyclopentadienyl-C(2, 5)), 83.7 (cyclopentadienyl-C(3, 4)), 49.1 (NCH_2), 22.9 ($=C(CH_3)$), 14.2 (cyclopentadienyl-CH_3) ppm.

Preparation of dicarbonyl[(E,Z)-N-2-furfuryl-N-methylamino-(2-propenyl)carbene](methylcyclopentadienyl)manganese (5)

A solution of 0.463 g (1.36 mmol) **4** in 5 ml tetrahydrofuran was added at −78 °C drop by drop to a solution of lithium diisopropylamide prepared from 0.23 ml (1.63 mmol) diisopropylamine and 1.02 ml (1.63 mmol) of a 1.6 M n-butyllithium solution in 30 ml tetrahydrofuran. After 1 h 0.10 ml (1.63 mmol) methyl iodide was added and the reaction mixture was allowed to warm to room temperature overnight. After removal of the solvent and purification by chromatography on silica gel using petroleum ether/diethyl ether 8/1 at −10 °C 0.39 g (81%) **5** was obtained as a red–brown oil in a *E/Z*-isomer ratio of 3:1. *Anal.* Calc. for $C_{18}H_{20}MnNO_3$ (353.30): C, 61.19; H, 5.71; N, 3.96. Found: C, 60.23; H, 5.76; N, 3.88%. IR (ν(CO), petroleum ether): 1932 (s), 1870 (s) cm^{-1}. ^1H NMR (300 MHz, acetone-d^6): δ=7.61 (s, 1H, furyl-H(5), *Z*-isomer), 7.57 (s, 1H, furyl-H(5), *E*-isomer), 6.42-6.55 (m, 2H, furyl-H(3, 4)), 5.64, 5.53 (d, J=15.48 Hz, 2H, NCH_2, *Z*-isomer), 4.93 (s, 2H, NCH_2, *E*-isomer), 4.00–4.59 (m, 6H, cyclopentadienyl-H(2–5), $=CH_2$), 3.66 (s, 3H, NCH_3, *E*-isomer), 2.95 (s, 3H, NCH_3, *Z*-isomer), 1.95 (s, 3H, cyclopentadienyl-CH_3), 1.88 (s, 3H, $=C(CH_3)$, *Z*-isomer), 1.85 (s, 2H, $=C(CH_3)$, *E*-isomer) ppm. ^{13}C NMR (75 MHz, acetone-d^6): *E*-isomer: δ=287.1 (carbene-C), 234.9 (CO), 155.8 (furyl-C(2)), 150.3 (=C(2)), 144.0 (furyl-C(5)), 111.5 (furyl-C(3)), 110.3 (furyl-C(4)), 102.3 (=C(1)), 100.4 (cyclopentadienyl-C(1)), 85.0, 84.9, 83.7, 83.0 (cyclopentadienyl-C(2–5)), 53.2 (NCH_3), 46.5 (NCH_2), 22.0 ($=C(CH_3)$), 14.0 (cyclopentadienyl-CH_3) ppm; *Z*-isomer: δ=287.1 (carbene-C), 234.9 (CO), 156.3 (furyl-C(2)), 150.6 (=C(2)), 144.0 (furyl-C(5)), 111.6 (furyl-C(3)), 110.6 (furyl-C(4)), 101.7 (=C(1)), 100.4 (cyclopentadienyl-C(1)), 83.8, 83.7, 83.5, 82.5 (cyclopentadienyl-C(2–5)), 58.5 (NCH_3), 40.8 (NCH_2), 20.8 ($=C(CH_3)$), 14.0 (cyclopentadienyl-CH_3) ppm.

Preparation of dicarbonyl[(E,Z)-N-benzyl-N-2-furfurylamino-)2-propenyl)carbene](methylcyclopentadienyl)manganese (6)

Analogous to the preparation of **5**, the reaction of 1.3 g (3.8 mmol) of complex **4** with 2.85 ml (4.56 mmol) of 1.6 M n-butyllithium, 0.63 ml (4.56 mmol) diisopropylamine and 0.54 ml (4.56 mmol) benzylbromide gave 1.42 g (87%) of a red–brown oil containing *E/Z*-isomers of **6** in a 2/1 ratio. *Anal.* Calc. for $C_{24}H_{24}MnNO_3$ (429.40): C, 67.13; H, 5.63; N, 3.26. Found: C, 67.19; H, 5.63; N, 3.26%. IR (ν(CO), petroleum ether): 1934 (s), 1873 (s) cm^{-1}. ^1H NMR (300 MHz, acetone-d^6): δ=7.15–7.72 (m, 6H, C_6H_5 and furyl-H(5)), 6.23–6.41 (m, 2H, furyl-H(3, 4)), 5.71, 5.15 (d, J=14.86 Hz, 2H, phenyl-CH_2, *Z*-isomer), 5.53, 5.34 (d, J=14.68 Hz, 2H, furyl-CH_2, *Z*-isomer), 4.07–4.94 (m, 6H and 4H-*E*-isomer, cyclopentadienyl-H(2–5), $=CH_2$, phenyl-NCH_2, *E*-isomer, furyl-NCH_2, *E*-isomer), 1.87 (m, 3H, cyclopentadienyl-CH_3), 1.83 (s, 3H, $=C(CH_3)$) ppm. ^{13}C NMR (75 MHz, acetone-d^6): *E*-isomer: δ=292.0 (carbene-C), 234.5 (CO), 155.9 (furyl-C(2)), 149.7 (=C(2)), 143.9 (furyl-C(5)), 136.9 (phenyl-C(1)), 129.7 (phenyl-C(3, 5)), 128.7 (phenyl-C(2, 6)), 128.0 (phenyl-C(4)), 111.4 (furyl-C(3)), 110.4 (furyl-C(4)), 102.5 (=C(1)), 100.2 (cyclopentadienyl-C(1)), 85.1, 84.9, 83.7, 82.9 (cyclopentadienyl-C(2–5), 61.8 (phenyl-NCH_2), 49.1 (NCH_2), 22.2 ($=C(CH_3)$), 14.0 (cyclopentadienyl-CH_3) ppm; *Z*-isomer: δ=291.3 (carbene-C), 234.5 (CO), 156.0 (furyl-C(2)), 150.1 (=C(2)), 143.4 (furyl-C(5)), 136.5 (phenyl-C(1)), 129.7 (phenyl-C(3, 5)), 128.7 (phenyl-C(2, 6)), 128.0 (phenyl-C(4)), 111.5 (furyl-C(3)), 110.7 (furyl-C(4)), 102.4 (=C(1)), 99.4 (cyclopentadienyl-C(1)), 85.4, 84.7, 84.3, 84.1 (cyclopentadienyl-C(2–5), 56.6 (phenyl-NCH_2), 54.9 (furyl-NCH_2), 21.8 ($=C(CH_3)$), 13.9 (cyclopentadienyl-CH_3) ppm.

Preparation of N-2-furfuryl-methacrylamide (7)

To a solution of 15.0 ml (156 mmol) methacrylic acid chloride in 150 ml dichloromethane, 21.8 ml (156 mmol) triethylamine and 13.8 ml (156 mmol) 2-furfurylamine were added successively at 0 °C. After stirring

for 1 h at room temperature, the solvent was removed at reduced pressure and purification by chromatography on silica gel using dichloromethane/petroleum ether (2/1) gave 24.0 g (93%) **7** as a white solid. *Anal.* Calc. for $C_9H_{11}NO_2$ (165.19): C, 65.44; H, 6.80; N, 8.48. Found: C, 65.41; H, 6.71; N, 8.40%. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.31$ (dd, $J = 0.86$, 1.85 Hz, 1H, furyl-H(5)), 6.27 (dd, $J = 1.87$, 3.22 Hz, 1H, furyl-H(4)), 6.19 (dd, $J = 0.62$, 3.26 Hz, 1H, furyl-H(3)), 6.10 (s, 1H, NH), 5.66 (s, 1H, =CH(*Z*)), 5.30 (q, $J = 1.35$ Hz, 1H, =CH(*E*)), 4.44 (d, $J = 5.51$ Hz, 2H, CH_2), 1.92 (d, $J = 1.19$ Hz, 3H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 167.9$ (C=O), 151.1 (furyl-C(2)), 142.1 (furyl-C(5)), 139.6 (=C(2)), 119.7 (=C(1)), 110.4 (furyl-C(3)), 107.4 (furyl-C(4)), 36.6 (CH_2), 18.5 (CH_3) ppm.

Preparation of N-2-furfuryl-N-methyl-methacrylamide (8)

Analogous to the preparation of **2**, 0.74 g (31 mmol) sodium hydride and 1.5 ml (23.2 mmol) methyl iodide were added to a solution of 2.57 g (15.5 mmol) **7** in 30 ml tetrahydrofuran. Purification by chromatography using dichloromethane/petroleum ether (2/1) afforded 2.67 g (96%) **8**. *Anal.* Calc. for $C_{10}H_{13}NO_2$ (179.22): C, 67.02; H, 7.31; N, 7.82. Found: C, 67.00; H, 7.35; N, 7.81%. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.32$ (s, 1H, furyl-H(5)), 6.28 (d, $J = 3.00$ Hz, 1H, furyl-C(4)), 6.21 (d, $J = 3.15$ Hz, 1H, furyl-C(3)), 5.18 (s, 1H, =CH(*Z*)), 5.07 (s, 1H, =CH(*E*)), 4.51 (s, 2H, CH_2), 2.89 (s, 3H, NCH_3), 1.94 (s, 3H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 172.4$ (C=O), 149.5 (furyl-C(2)), 142.4 (furyl-C(5)), 139.8 (=C(2)), 115.8 (=C(1)), 110.1 (furyl-C(3)), 108.3 (furyl-C(4)), 44.8 (CH_2), 33.9 (NCH_3), 20.5 (CH_3) ppm.

Preparation of N-benzyl-N-2-furfuryl-methacrylamide (9)

As described above, the reaction of 2.57 g (15.5 mmol) **7** in 30 ml of tetrahydrofuran, 0.74 g (31 mmol) sodium hydride and 2.75 ml (23.2 mmol) of benzylbromide gave 2.69 g (68%) **9**. *Anal.* Calc. for $C_{16}H_{17}NO_2$ (255.32): C, 75.27; H, 6.71; N, 5.49. Found: C, 75.10; H, 6.72; N, 5.88%. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.26$ (m, 6H, phenyl-H, furyl-H(5)), 6.34 (d, $J = 3.00$ Hz, 1H, furyl-H(4)), 6.20 (d, $J = 3.15$ Hz, 1H, furyl-H(3)), 5.22 (s, 1H, =CH(*Z*)), 5.20 (s, 1H, =CH(*E*)), 4.54 (s, 2H, furyl-CH_2), 5.48 (s, 2H, phenyl-CH_2), 2.04 (s, 3H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 172.8$ (C=O), 149.4 (furyl-C(2)), 142.3 (furyl-C(5)), 139.8 (=C(2)), 136.1 (phenyl-C(1)), 128.7–126.6 (phenyl-C(2–6)), 115.8 (=C(1)), 110.1 (furyl-C(3)), 109.0 (furyl-C(4)), 48.1 (phenyl-CH_2), 41.3 (furyl-CH_2), 21.0 (CH_3) ppm.

Preparation of pentacarbonyl[(3aS,6R*,7aR*)-(2,7a-dimethyl-1,3,3a,6,7,7a-hexahydro-3a,6-epoxy-3aH-isoindol)-1-ylidene]tungsten (11)*

0.487 g (1.00 mmol) **2** was heated at 90 °C in 10 ml toluene for 3 h. The solvent was removed at reduced pressure and chromatography on silica gel using diethyl ether/petroleum ether (2/1) as eluent gave 0.453 g (93%) **11** as a yellow solid. *Anal.* Calc. for $C_{15}H_{13}NO_6W$ (487.12): C, 36.98; H, 2.69; N, 2.88. Found: C, 36.89; H, 2.74; N, 2.68%. IR (ν(CO), petroleum ether): 2062 (m), 1965 (sh), 1928 (vs), 1915 (s) cm^{-1}. ^{1}H NMR (300 MHz, acetone-d^6): $\delta = 6.54$ (d, $J = 5.78$ Hz, 1H, H(5)), 6.50 (d, $J = 5.67$ Hz, 1H, H(4)), 4.96 (d, $J = 4.78$ Hz, 1H, H(6)), 4.56, 4.08 (d, $J = 14.27$ Hz, 2H, CH_2(3)), 3.71 (s, 3H, NCH_3), 2.71 (dd, $J = 4.92$, 11.67 Hz, 1H, H(7)-*trans*-H(6)), 1.48 (d, $J = 11.69$ Hz, 1H, H(7)-*cis*-H(6)), 1.06 (s, 3H, CH_3) ppm. ^{13}C NMR (75 MHz, acetone-d^6): $\delta = 257.0$ (carbene-C), 203.4 (*trans*-CO), 199.7 (*cis*-CO), 139.3 (C(4)), 132.9 (C(5)), 94.3 (C(3a)), 79.7 (C(6)), 76.4 (C(7a)), 62.2 (C(3)), 45.8 (NCH_3), 40.4 (C(7)), 23.0 (CH_3) ppm.

Preparation of pentacarbonyl[(3aS,6R*,7aR*)-(2-benzyl-7a-methyl-1,3,3a,6,7,7a-hexahydro-3a,6-epoxy-3aH-isoindol)-1-ylidene]tungsten (12)*

As described above for **11**, 0.247 g (65%) **12** was obtained from 0.38 g (0.67 mmol) **3** as a yellow solid. *Anal.* Calc. for $C_{21}H_{17}NO_6W$ (563.22): C, 44.78; H, 3.04; N, 2.49. Found: C, 44.81; H, 3.17; N, 2.36%. IR (ν(CO), petroleum ether): 2062 (m), 1965 (w), 1930 (vs), 1915 (s) cm^{-1}. ^{1}H NMR (300 MHz, acetone-d^6): $\delta = 7.39$ (m, 5H, phenyl-H), 6.57 (dd, $J = 1.66$, 5.76 Hz, 1H, H(5)), 6.52 (d, $J = 5.77$ Hz, 1H, H(4)), 5.53, 5.28 (d, $J = 15.56$ Hz, 2H, phenyl-CH_2), 5.04 (dd, $J = 1.70$, 4.94 Hz, 1H, H(6)), 4.42, 3.98 (d, $J = 14.23$ Hz, 2H, CH_2(3)), 2.86 (dd, $J = 4.95$, 11.75 Hz, 1H, H(7)-*trans*-H(6)), 1.60 (d, $J = 11.76$ Hz, 1H, H(7)-*cis*-H(6)), 1.17 (s, 3H, CH_3) ppm. ^{13}C NMR (75 MHz, acetone-d^6): $\delta = 260.7$ (carbene-C), 203.1 (*trans*-CO), 199.6 (d, $J = 125.25$ Hz, *cis*-CO), 139.4 (C(4)), 134.9 (phenyl-C(1)), 132.8 (C(5)), 129.8 (phenyl-C(3,5)), 128.9 (phenyl-C(4)), 94.2 (C(3a)), 79.9 (C(6)), 76.4 (C(7a)), 61.2 (C(3)), 59.4 (phenyl-CH_2), 41.0 (C(7)), 23.1 (CH_3) ppm.

Preparation of dicarbonyl[(7a-methyl-1,3,3a,6,7,7a-hexahydro-3a,6-epoxy-isoindol)-1-ylidene](methylcyclopentadienyl)manganese (13)

A solution of 0.56 g (1.70 mmol) **4** was warmed at 80 °C in 10 ml toluene for 24 h. Removal of the solvent and purification by chromatography on silica gel using petroleum ether/diethyl ether (1/4) as eluent at −10 °C gave 0.27 g (48%) **13** as a yellow solid. *Anal.* Calc. for $C_{17}H_{18}MnNO_3$ (339.27): C, 60.18; H, 5.35; N, 4.13. Found: C, 59.97; H, 5.43; N, 3.96%. IR (ν(CO), petroleum ether): 1927 (s), 1864 (s) cm^{-1}. ^{1}H NMR (300

MHz, acetone-d^6): δ=9.35 (s, 1H, NH), 6.48 (s, 2H, H-4, 5), 4.87 (d, J=4.72 Hz, 1H, H(6)), 4.36–4.53 (m, 4H, cyclopentadienyl-H(2–5)), 3.77, 4.09, (d, J=13.10 Hz, 2H, CH_2(3)), 2.62 (dd, J=4.85, 11.71 Hz, 1H, H(7)-*trans*-H(6)), 1.83 (s, 3H, cyclopentadienyl-CH_3), 1.44 (J=11.73 Hz, 1H, H(7)-*cis*-H(6)), 0.98 (s, 3H, CH_3) ppm. ^{13}C NMR (75 MHz, acetone-d^6): δ=290.0 (carbene-C), 236.0 (CO), 138.6 (C(4)), 133.6 (C(5)), 101.1 (cyclopentadienyl-C(1)), 94.8 (C(3a)), 83.7, 83.2, 82.9, 82.3 (cyclopentadienyl-C(2–5)), 79.6 (C(6)), 72.0 (C(7a)), 54.2 (C(3)), 40.0 (C(7)), 23.0 (CH_3), 14.0 (cyclopentadienyl-CH_3) ppm.

Preparation of dicarbonyl[(2,7a-dimethyl-1,3,3a,6,7,7a-hexahydro-3a,6-epoxy-isoindol)-1-ylidene](methylcyclopentadienyl)manganese (14)

A solution of 0.26 g (0.70 mmol) **5** was warmed at 80 °C in 10 ml toluene for 6 h. Removal of the solvent and purification by chromatography on silica gel using petroleum ether/diethyl ether (1/4) as eluent at −10 °C gave 0.19 g (72%) **14** as a yellow solid. *Anal.* Calc. for $C_{18}H_{20}MnNO_3$ (353.30): C, 61.19; H, 5.71; N, 3.96. Found: C, 61.10; H, 5.83; N, 4.01%. IR (ν(CO), petroleum ether): 1928 (s), 1865 (s) cm^{-1}. ^{1}H NMR (300 MHz, acetone-d^6): δ=6.48 (m J=1.35 Hz, 2H, H(4, 5)), 4.48 (dd, J=1.30, 4.77 Hz, 1H, H(6)), 4.22–4.36 (m, 4H, cyclopentadienyl-H(2–5)), 3.88, 4.36 (d, J=13.49 Hz, 2H, H(3)), 3.61 (s, 3H, NCH_3), 2.81 (dd, J=11.82 Hz, 1H, H(7)-*trans*-H(6)), 1.47 (d, J=11.82 Hz, 1H, H(7)-*cis*-H(6)), 1.79 (s, 3H, cyclopentadienyl-CH_3), 0.98 (s, 3H, CH_3) ppm. ^{13}C NMR (75 MHz, acetone-d^6): δ=287.0 (carbene-C), 236.0 (C)), 139.0 (C(4)), 133.3 (C(5)), 101.0 (cyclopentadienyl-C(1)), 94.2 (C(3a)), 83.4, 82.9, 82.2, 81.6 (cyclopentadienyl-C(2-5)), 79.6 (C(6)), 74.4 (C(7a)), 61.2 (C(3)), 42.3 (NCH_3), 40.7 (C(7)), 22.6 (CH_3), 13.8 (cyclopentadienyl-CH_3) ppm.

Preparation of dicarbonyl[(2-benzyl-7a-methyl-1,3,3a,6,7,7a-hexahydro-3a,6-epoxy-isoindol)-1-ylidene](methylcyclopentadienyl)manganese (15)

A solution of 0.50 g (0.70 mmol) **6** in 10 ml toluene was warmed at 80 °C for 4 h. Removal of the solvent and purification by chromatography on silica gel using petroleum ether/diethyl ether (1:1) as eluent at −10 °C gave 0.38 g (75%) **15** as a yellow solid. *Anal.* Calc. for $C_{24}H_{24}MnNO_3$ (429.40): C, 67.13; H, 5.63; N, 3.26. Found: C, 66.94; H, 5.86; N, 3.08%. IR (ν(CO), petroleum ether): 1926 (s), 1864 (s) cm^{-1}. ^{1}H NMR (300 MHz, acetone-d^6): δ=7.33–7.43 (m, 5H, phenyl-H), 6.39–6.45 (m, 2H, H(4, 5)), 5.78, 4.92 (d, J=14.40 Hz, 2H, phenyl-CH_2), 4.86 (m, 1H, H(6)), 4.26–4.30 (m, 4H, cyclopentadienyl-H(2–5)), 3.84, 3.70 (d, J=13.12 Hz, 2H, H(3)), 2.85 (dd, J=11.51, 4.47 Hz, 1H, H(7)-*trans*-H(6)), 1.83 (s, 3H, cyclopentadienyl-CH_3), 1.51 (d, J=11.69 Hz, 1H, H(7)-*cis*-H(6)), 0.97 (s, 3H, CH_3) ppm. ^{13}C NMR (75 MHz, acetone-d^6): δ=290.0 (carbene-C), 236.0 (CO), 139.2 (C-4), 136.7 (phenyl-C(1)), 133.4 (C(5)), 129.8 (phenyl-C(3, 5)), 129.2 (phenyl-C(2, 6)), 128.8 (phenyl-C(4)), 100.9 (cyclopentadienyl-C(1)), 94.0 (C(3a)), 83.8, 83.3, 82.5, 82.0 (cyclopentadienyl-C(2–5)), 79.9 (C(6)), 74.3 (C(7a)), 59.3 (C(3)), 58.0 (phenyl-CH_2), 41.1 (C(7)), 22.6 (CH_3), 14.0 (cyclopentadienyl-CH_3) ppm.

Preparation of (3aS,6R*,7aR*)-2-benzyl-7a-methyl-1-oxo-1,3,3a,6,7,7a-hexahydro-3a,6-epoxy-3aH-isoindol (18)*

A solution of 1.00 g (3.920 mmol) **9** in 50 ml toluene was refluxed for 6 h. Removal of the solvent and purification by chromatography on silica gel using diethyl ether as eluent at −10 °C gave 0.89 g (89%) **18** as a colorless liquid. *Anal.* Calc. for $C_{16}H_{17}NO_2$ (255.32): C, 75.27; H, 6.71; N, 5.49. Found: C, 75.48; H, 6.65; N, 5.36%. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.19 (m, 5H, phenyl-H), 6.36 (dd, J=1.77, 5.85 Hz, 1H, H(5)), 6.24 (d, J=5.82 Hz, 1H, H(4)), 4.78 (dd, J=1.63, 4.75 Hz, 1H, H(6)), 4.54, 4.31 (d, J=15.02 Hz, 2H, phenyl-CH_2), 3.64, 3.41 (d, J=11.75 Hz, 2H, CH_2(3)), 2.40 (dd, J=11.75 Hz, 1H, H(7)-*trans*-H(6)), 1.04 (d, J=11.75 Hz, 1H, H(7)-*cis*-H(6)), 0.98 (s, 3H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ=177.6 (C(1)), 137.4 (C(4)), 136.2 (phenyl-C(1)), 131.4 (C(5)), 128.6 (phenyl-C(3, 5)), 127.7 (phenyl-C(2, 6)), 127.4 (phenyl-C(4)), 91.0 (C(3a)), 78.7 (C(6)), 52.0 (C(7a)), 47.4 (C(3)), 46.3 (phenyl-CH_2), 35.9 (C(7)), 20.4 (CH_3) ppm.

Comparative studies of the cyclization reactions

0.50 mmol of the educts **1–9** and, in the case of the methacrylamides, equimolar amounts of Lewis acids (titanium tetrachloride or diethyl aluminum chloride) were dissolved in 10 ml toluene and warmed at 80 °C (**4–6**) or at 90 °C (**1–3**, **7–9**) for 3 h. If Lewis acids were used (see Table 1), the reaction mixture was hydrolyzed by 5 ml water at 0 °C. The organic layer was separated and dried over molecular sieve 3 Å. After removal of the solvent at reduced pressure the degree of conversion was detected by ^{1}H NMR spectra of the residue.

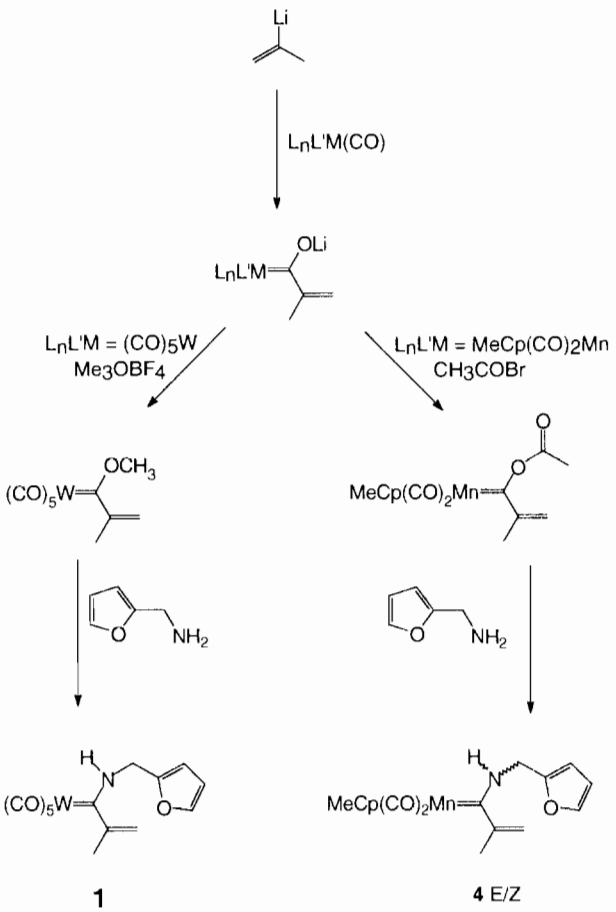
Results and discussion

Synthesis of diene-dienophile-functionalized carbene complexes

Our synthesis of diene-dienophile substituted carbene complexes is based on a two-step functionalization process starting from metal carbonyl precursors. The classical Fischer route involving sequential addition of a 2-lithiopropene nucleophile and a carbon electrophile across a carbonyl ligand provides an oxycarbene ligand

containing the dienophile. Subsequently, the diene moiety is incorporated by aminolysis using furfurylamine. In order to study the role of the activating metal fragment in the [4+2] cycloaddition we have focussed on the hexacarbonyl tungsten and the tricarbonyl(methylcyclopentadienyl)manganese series in which the metal centers distinctly differ in their electron acceptor capacities with respect to the carbene ligand.

While both the preparation of the methoxy(2-propenyl)carbene tungsten complex using $Me_3O^+BF_4^-$ as alkylating agent and its aminolysis occurred straightforwardly to give pentacarbonyl complex **1**, a similar approach to the manganese analogue **4** has to face the reduced acceptor ability of the $MeCp(CO)_2Mn$ fragment making the modification of a carbonyl ligand to the aminocarbene species, which is based on a double nucleophilic attack, less favorable. Accordingly, the methoxy(2-propenyl)carbene manganese complex could be obtained only in yields not exceeding 10%. In order to facilitate the addition of the diene nucleophile the methoxy intermediate was substituted for the more electrophilic acetyloxycarbene complex. Its preparation from tricarbonyl(methylcyclopentadienyl)manganese, 2-lithiopropene and acetyl bromide was supported by the presence of the Li^+-chelating additive TMEDA both in the nucleophilic addition and acylation step. The acyloxycarbene complex was reacted *in situ* with furfurylamine to give a 35% yield of **4** which, in contrast to the synthesis of **1**, was obtained in a 3/1 mixture of *E*/*Z*-isomers (Scheme 2). The propensity of *N*-furfurylamino acrylic amides to undergo intramolecular [4+2] cycloaddition is known to depend on further N-substitution [14]. In order to probe for similar effects in the aminocarbene series the secondary aminocarbene ligands in **1** and **4** were modified into the tertiary homologues by methylation or benzylation (Scheme 3). In the tungsten series, *N*–H deprotonation was achieved by sodium hydride at 0 °C, and subsequent alkylation using methyl iodide or benzyl bromide afforded compounds **2** and **3** in 90 and 63% yield, respectively. Starting from the manganese analogue **4**, a similar deprotonation methodology failed. Again, this may be rationalized in terms of the less effective electron withdrawing property of the manganese coligand fragment resulting in a less efficient stabilization of the anion derived from **4** and thus reducing the *N*–H acidity of the secondary aminocarbene substituent. The different acceptor properties of both metal fragments are evident from their ^1H NMR spectra: in the tungsten complex **1**, the *N*–H hydrogen atom resonates at 10.77 ppm, while chemical shifts of 9.54 and 9.35 ppm, respectively, are observed for the *E*/*Z*-isomers of the manganese complex **4**.



Scheme 2.

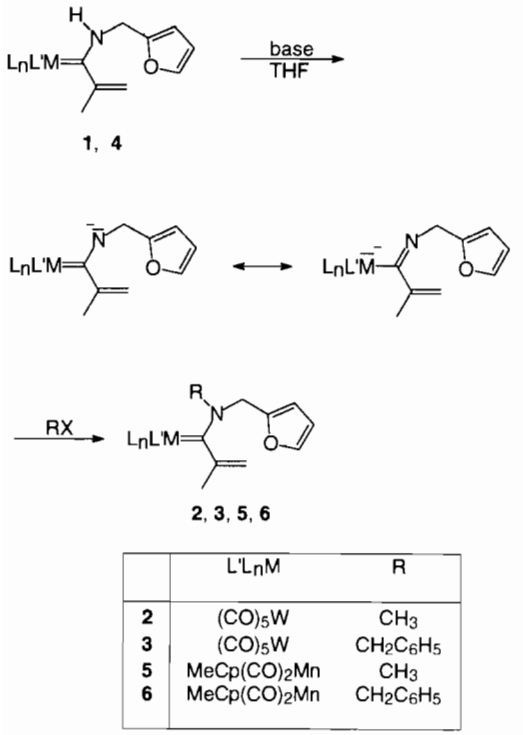
Intramolecular Diels–Alder reactions

When the tungsten complex **1** is warmed in toluene cyclization occurs to give the epoxy-3aH-isoindolylidene complex **10**. The reaction is stereospecific; only one diastereomer arising from a *trans* fusion of the newly formed five-membered rings is obtained as has been established by X-ray analysis [12]. The same stereochemistry is observed for the Diels–Alder products derived from the *N*-methyl and *N*-benzyl homologues as established by a comparison of ^1H and ^{13}C NMR spectra. Comparative reactivity studies indicate that the propensity for ring closure increases with increasing bulk of N-substitution (Scheme 4, Table 1). While – based on quantitative ^1H NMR studies – the secondary aminocarbene complex **1** leads to a 79% conversion to the cycloadduct **10** after warming a toluene solution to 90 °C for 3 h, complete conversion occurs with the methyl or benzyl analogues **2** and **3** under identical conditions. A similar trend is obvious from the manganese series. When a 0.17 M solution of the secondary aminocarbene complex **4** in toluene is warmed to 80 °C the conversion does not exceed 48% after 24 h. In comparison 0.07 M solutions of the *N*-methyl and *N*-benzyl derivatives **5** and **6** lead to a 72 and 75%

TABLE 1. Reaction conditions of the intramolecular Diels–Alder reactions of the compounds **1–9** (see Scheme 4)

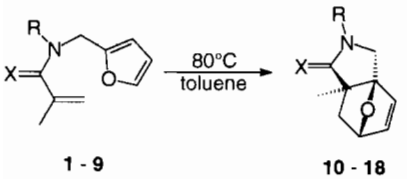
Educt	X	R	Lewis acid	Conditions (h/°C)	Product	Conversion[a] (%)
1	$(CO)_5W$	H		3/90	**10**	79
2	$(CO)_5W$	CH_3		3/90	**11**	100
3	$(CO)_5W$	$CH_2C_6H_5$		3/90	**12**	100
4	$MeCp(CO)_2Mn$	H		24/80	**13**	48[b]
5	$MeCp(CO)_2Mn$	CH_3		6/80	**14**	72[b]
6	$MeCp(CO)_2Mn$	$CH_2C_6H_5$		4/80	**15**	75[b]
7	O	H		3/90	**16**	0
7	O	H	Et_2AlCl	3/90	**16**	0
7	O	H	$TiCl_4$	3/90	**16**	0
8	O	CH_3		3/90	**17**	27
8	O	CH_3	$TiCl_4$	3/90	**17**	0
8	O	CH_3	Et_2AlCl	3/90	**17**	10
9	O	$CH_2C_6H_5$		3/90	**18**	36
9	O	$CH_2C_6H_5$	$TiCl_4$	3/90	**18**	27
9	O	$CH_2C_6H_5$	Et_2AlCl	3/90	**18**	79

[a]From ^1H NMR. [b]Isolated yields.



	L'LnM	R
2	$(CO)_5W$	CH_3
3	$(CO)_5W$	$CH_2C_6H_5$
5	$MeCp(CO)_2Mn$	CH_3
6	$MeCp(CO)_2Mn$	$CH_2C_6H_5$

Scheme 3.



Scheme 4.

conversion after 6 and 4 h, respectively. These results can be rationalized by the assumption that bulky N-substitution favors the conformation within the furfuryl group required for cyclization. They are consistent with earlier observations reported for acrylic furfuryl amides [14].

A comparison of homologous manganese and tungsten complexes (Table 1) further indicates that the propensity for intramolecular Diels–Alder reaction increases with increasing acceptor capacity of the metal fragment. Results obtained from intermolecular [4+2] cycloadditions [11] suggest that the electron withdrawing properties of the $(CO)_5M$ moiety (M = Cr or W) is at least similar to that of a Lewis acid coordinated oxygen atom.

Even the less effective acceptor fragment $MeCp(CO)_2Mn$ is distinctly more efficient in [4+2] cycloadditions than the isolobal oxygen atom. The methacrylic furfuryl amide **7** is inert towards cyclization when warmed in toluene to 90 °C for 3 h; even in the presence of an equimolar amount of a Lewis acid such as titanium tetrachloride or diethylaluminum chloride no trace of Diels–Alder product **16** could be detected. As indicated in the metal carbene series the cyclization is favored by an increasing bulk of N-substitution. Under identical conditions (3 h, 90 °C) the conversion slightly increases in the order **7** (R = H), **8** (R = methyl) and **9** (R = benzyl). The results obtained in the presence of Lewis acids are not straightforward. The addition of both $TiCl_4$ and Et_2AlCl to a toluene solution of the methyl derivative **8** decreases the propensity for cyclization; on the other hand the conversion of the benzyl analogue **9** is enhanced by addition of the aluminum reagent, but slightly decreases in the presence of the titanium additive (Table 1).

Acknowledgements

Support for this work by the Deutsche Forschungsgemeinschaft (SFB 260), the Graduiertenkollegs 'Metallorganische Chemie' and 'Spektroskopie isolierter und kondensierter Moleküle' as well as by the Fonds der Chemischen Industrie is gratefully acknowledged.

References

1 J. Christoffers and K.H. Dötz, *J. Chem. Soc., Chem. Commun.,* (1993) 1811.
2 K.H. Dötz, H. Fischer, P. Hofmann, F.R. Kreißl, U. Schubert and K.Weiß, *Transition Metal Carbene Complexes,* Verlag Chemie, Weinheim, 1983.
3 K.H. Dötz, *Angew. Chem., Int. Ed. Eng., 23* (1984) 587.
4 L.S. Hegedus, *Pure Appl. Chem., 62* (1990) 691.
5 W.D. Wulff, in B.M. Trost and I. Fleming (eds.), *Comprehensive Organic Synthesis,* Vol. 5, Pergamon, New York, 1991, p. 1065 ff.
6 K.H. Dötz, in H. tom Dieck and A. de Meijere (eds.), *Organometallics in Organic Synthesis: Aspects of a Modern Interdisciplinary Field,* Springer, Berlin 1988.
7 (a) C.G. Kreiter, *Angew. Chem., Int. Ed. Engl., 7* (1968) 390; (b) C.P. Casey and R.L. Anderson, *J. Am. Chem. Soc., 96* (1974) 1230.
8 W.D. Wulff, B.A. Anderson and A.J. Toole, *J. Am. Chem. Soc., 111* (1989) 5485.
9 B.A. Anderson, W.D. Wulff and A. Rahm, *J. Am. Chem. Soc., 115* (1993) 4602.
10 (a) R. Hoffmann, *Angew. Chem., Int. Ed. Engl., 21* (1982) 711; (b) F.G.A. Stone, *Angew. Chem., Int. Ed. Engl., 23* (1984) 89.
11 (a) W.D. Wulff and D.C. Yang, *J. Am. Chem. Soc., 105* (1983) 6726; (b) K.H. Dötz and W. Kuhn, *J. Organomet. Chem., 286* (1985) C23–C26; (c) W.D. Wulff, W.E. Bauta, R.W. Kaesler, P.J. Lankford, R.A. Miller, C.K. Murray and D.C. Yang, *J. Am. Chem. Soc., 112* (1990) 3642; (d) W.D. Wulff and T.S. Powers, *J. Org. Chem., 58* (1993) 2381.
12 K.H. Dötz, R. Noack, K. Harms and G. Müller, *Tetrahedron, 46* (1990) 1235.
13 (a) E. Ciganek, *Org. React., 32* (1984) 1; (b) D.F. Taber, *Intramolecular Diels–Alder and Alder Ene Reactions,* Springer, Berlin, 1984; (c) W. Oppolzer, *Angew. Chem., Int. Ed. Engl., 16* (1977) 10; *23* (1984) 876; (d) A.G. Fallis, *Can. J. Chem., 62* (1984) 183.
14 K.A. Parker and M.R. Adamchuk, *Tetrahedron Lett.,* (1978) 1689.