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Chemoselective Diels–Alder reactions of a non-symmetrical bis(carbene)-bridged ditungsten complex with 1,3-dienes

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Abstract

The non-symmetrical [(dimethylamino)alkenylcarbene-(methoxy)alkenylcarbene] ditungsten complex **2** undergoes Diels–Alder reactions with 2,3-dimethyl-1,3-butadiene and cyclopentadiene that proceed selectively at the methoxycarbene ligand. Similar Diels–Alder cycloadditions with the symmetrical bis[(methoxy)alkenylcarbene]ditungsten complex **1** are reported for comparison.

Keywords: Tungsten; Carbene complexes; Bridging ligands; Diels–Alder reactions

1. Introduction

We recently reported that binuclear alkenylcarbene-bridged complexes can be conveniently prepared by sequential activation of bis(propargyl alcohol) derivatives [1]. This procedure allows the access to non-symmetrical bis(carbene) complexes containing two different tungsten–carbene fragments, the (alkoxy)- and (amino)carbene ligands. It is well established that the reactivity of alkenylcarbene complexes depends on the nature of the metal but also on that of the substituent (alkoxy vs. amino) in classical reactions such as annulation reactions and Diels–Alder cycloadditions [2–4]. For example group 6 (alkoxy)alkenylcarbene complexes behave as very reactive and mainly *endo*-selective dienophiles in [4+2] cycloaddition reactions [5–8]. On the other hand, the replacement of the alkoxy group by a dialkylamino group leads to a dramatic decrease in reactivity toward 1,3 dienes, due to the better stabilizing effect of NR_2 versus OR. [9]. This difference in behaviour should also be expected in bimetallic complexes such as **2** featuring a methoxy–alkenyl and a dimethylamino–alkenyl moieties (Scheme 1). In this communication we will focus on the chemoselective Diels–Alder cycloaddition of 2,3-dimethyl-1,3-butadiene and cyclopentadiene to **2**. For comparison, the same reaction is also described with the symmetrical bis(methoxycarbene)ditungsten derivative **1**.

2. Results and discussion

We first studied the reaction of the symmetrical complex **1** with 2,3-dimethyl-1,3-butadiene (Scheme 2). Our initial attempt, carried out at room temperature, resulted in no reaction, even after 3 days of stirring. As already mentioned by Wulff et al. [6], the presence of substituents on the double bond of the dienophile results in decreased reactivity toward dienes such as 2,3-dimethyl-1,3-butadiene. However, at 50 °C and after 18 h of stirring, the initially purple solution became slowly orange–red, a colour change characteristic of the formation of nonconjugated (methoxy)carbene complexes. Chromatographic workup at this stage gave the expected bis-cycloadduct **3** in 35% yield along with the starting carbene complex (20%).

Compound **3** is isolated as a single isomer in which the phenylene substituent and the organometallic fragment are *trans*, the configuration of the initial CH=CH double bond being unchanged. The assignment was

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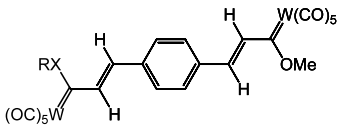
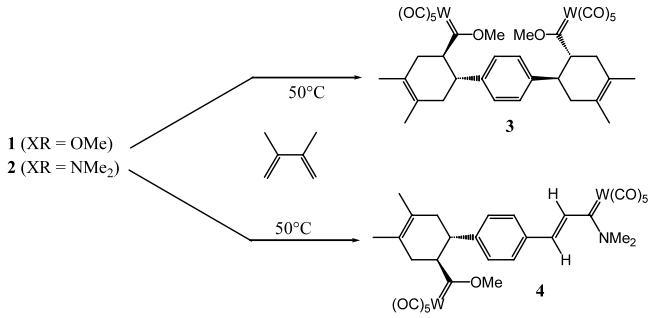


1 XR = OMe
2 XR = NMe_2

Scheme 1.



Scheme 2.

based on NMR data, the corresponding coupling constant of ca. 11 Hz is characteristic of axial hydrogens. It is noteworthy that the reaction is stereoselective, since two diasteroisomers are expected. We assume that the *meso* isomer, in which the two organometallic fragments are *cis* with respect to the phenylene plane, is sterically too hindered.

Next we examined the reaction of **2** with 2,3-dimethyl-1,3-butadiene under the same conditions, i.e. at 50 °C for 18 h. The reaction afforded only the mono-cycloadduct **4** in 28% isolated yield and again, the starting complex **2** was not totally consumed (30% of the starting complex was recovered after column chromatography). Thus, the Diels–Alder reaction, although uncomplete, is chemoselective and occurs specifically at the C=C of (methoxy)alkenylcarbene fragment.

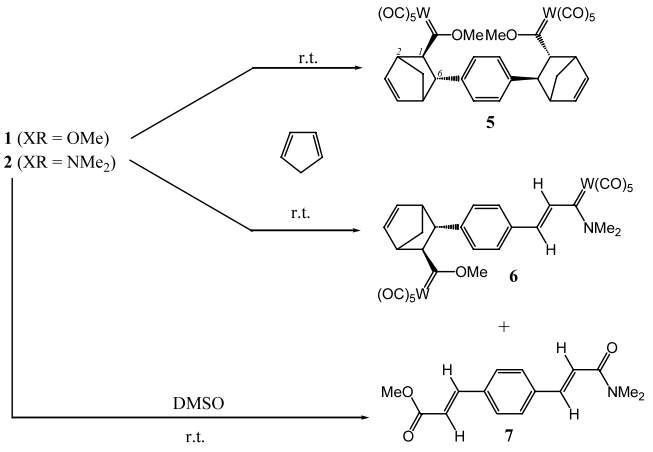
The structures of **3** and **4** could easily be inferred from spectroscopic data. For example, the ^{1}H-NMR spectrum of **4** reveals the characteristic two AB systems for the alkenyl protons of the (amino)carbene fragment. The resonance signals for the two carbene carbon atoms in the ^{13}C-NMR spectrum ($\delta_{RW=C} = 252.8$ and 343.8) compare well with those usually observed for (amino)alkenylcarbene and (methoxy)alkylcarbene complexes, respectively.

Selected data for **3**: (yield: 34%). ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 7.03$ (s, 4H, C_6H_4), 4.44 (td, 2H, ^3JH–H = 4.6 Hz, ^3JH–H_{aa} = 11 Hz, H^1), 4.38 (s, 6H, OMe), 2.95 (td, 2H, ^3JH–H = 5.2 Hz, ^3JH–H_{aa} = 11.4 Hz, H^6), 2.31 (m, 4H, ^3JH–H = 4.2 Hz, CH_2), 1.94 (m, 4H, CH_2), 1.65 (s, 6H, CH_3), 1.61 (s, 6H, CH_3). ^{13}C [^{1}H]-NMR (75.47 MHz, $CDCl_3$): $\delta = 343.7$ (=C), 203.1 (CO *trans*), 197.2 (CO *cis*), 129.3, 128.0, 127.6 (C_6H_4), 125.9 ($C^{3/4}$), 123.7 ($C^{3/4}$), 74.3 (C^1), 70.1 (OMe), 44.1 (C^6), 40.72 (CH_2), 36.7 (CH_2), 18.7 (CH_3), 18.6 (CH_3). IR (CH_2Cl_2, cm^{-1}): 2068 (m, νCO), 1939 (s, νCO). HRMS: *m/z* Found 942.1235. Calc. for $C_{33}H_{34}O_9W_2$ $[M+H]^+$ 942.1222.

Selected data for **4**: (yield: 26%). ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 7.26$ (d, 2H, ^3JH–H = 8.2 Hz, C_6H_4), 7.14 (d, 2H, ^3JH–H = 8.3 Hz, C_6H_4), 6.95 (d, 1H, ^3JH–H = 16.7 Hz, $=CH_\alpha$), 5.91 (d, 1H, ^3JH–H = 16.6 Hz, $=CH_\beta$), 4.43 (s, 3H, OMe), 4.42 (td, 1H, ^3JH–H = 4.7 Hz, ^3JH–H = 11.5 Hz, H^1), 3.80(s, 3H, NMe*Z*), 3.37 (s, 3H, NMe*E*), 3.00 (td, 1H, ^3JH–H = 5.2 Hz, ^3JH–H = 11.3 Hz, H^6), 2.31 (m, 2H, CH_2), 1.96 (m, 2H, CH_2), 1.64 (s, 6H, CH_3). ^{13} C [^{1}H]-NMR (75.47 MHz, $CDCl_3$): δ = 343.8 (W=*C*(O), 252.4 (W=*C*(N), 203.6, 203.2 (CO *trans*), 198.5, 197.1 (CO *cis*), 143.8 (C_6H_4), 138.2 (C^α), 134.1, 128.3, 126.5 (C_6H_4), 125.3 ($C^{3/4}$), 124.0 ($C^{3/4}$), 123.8 (C^β), 74.6 (C^1), 70.1 (OMe), 53.5 (NMe*Z*), 44.5 (NMe*E*), 44.2 (C^6), 39.9 (CH_2), 36.3 (CH_2), 18.8 (CH_3), 18.5 (CH_3). IR (CH_2Cl_2, cm^{-1}): 2069, 2061 (m, νCO), 1926 (s, νCO). HRMS: *m/z* Found 958.0645. Calc. for $C_{31}H_{28}NO_{11}W_2$ $[M+H]^+$ 958.0681.

The reaction of **1** and **2** with cyclopentadiene was then investigated. The homobimetallic complex **1** reacted slowly (3 days) at room temperature to give bis-cycloadduct **5**, in a 65% total isolated yield after column chromatography. This new complex **5** consisted of a 83:17 mixture of *trans endo–endo* and *trans endo–exo* cycloadducts, which could not be separated, the *trans exo–exo* isomer not being observed, in line with the low expected yield (Scheme 3). The assignment of the endo stereochemistry was made on the basis of the coupling constants JH^{1}H^6 and$J$H^{1}H^2 as reported for the mono-adduct obtained for the reaction of methoxy–propenylcarbene tungsten complex with cyclopentadiene (*endo*:*exo* ratio 90:10) [6].

Under the same conditions, the reaction of **2** with cyclopentadiene resulted again in the formation of the mono-cycloadduct; complex **6** was obtained in 42% yield as a 81:19 mixture of *endo*:*exo* isomers.



Scheme 3.

The structures of these new complexes were determined by NMR spectroscopy and the assignment of the *endo* and *exo* isomers was done by comparison with the ^{1}H-NMR data of the related monometallic cycloadduct [6]. The demetalated compound **7**, resulting from the air oxidation of the starting complex **2**, was also isolated by column chromatography in 25% yield.

Selected data for **5** (*trans endo–endo*): (yield: 65%). ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 7.05$ (s, 4H, C_6H_4), 6.35 (dd, 2H, ^3JH–H = 3.2 Hz, ^3JH–H = 5.6 Hz, $H^{3/4}$), 5.78 (dd, 2H, ^3JH–H = 2.8 Hz, ^3JH–H = 5.5 Hz, $H^{3/4}$), 4.61 (dd, 2H, ^3JH–H = 3.2 and 4.9 Hz, H^1), 4.55 (s, 6H, OMe), 3.54 (m, 2H, $H^{2/}$ $H^{2/5}$), 2.99 (m, 4H, $H^{2/5}$and H^6), 1.53 (m, 4H, CH_2). ^{13} C [^{1}H]-NMR (50.32 MHz, $CDCl_3$): $\delta = 335.2$ (=C), 202.8 (CO *trans*), 197.4 (CO *cis*), 141.6 (C_6H_4), 139.1 ($C^{3/4}$), 137.1, 136.2 (C_6H_4), 132.7 ($C^{3/4}$), 126.9, 127.0 (C_6H_4), 82.1 (OMe), 70.8 (C_2), 50.5 (C^5), 49.9 ($C^{2/6}$), 48.9($C^{2/6}$), 47.9 (CH_2). IR (CH_2Cl_2, cm^{-1}): 2068 (m, νCO), 1937 (s, νCO). HRMS: *m/z* Found 994.0453. Calc. for $C_{34}H_{26}O_{12}W_2$ 994.0443.

Selected data for **6**: (yield: 35%). ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 7.32$ (d, 2H, ^3JH–H = 8.2 Hz, C_6H_4), 7.14 (d, 2H, ^3JH–H = 8.3 Hz, C_6H_4), 6.99 (d, 1H, ^3JH–H = 16.5 Hz, $=CH_\alpha$), 6.38 (dd, 1H, ^3JH–H = 3.2 Hz, ^3JH–H = 5.5 Hz, $H^{3/4}$), 5.95 (d, 1H, ^3JH–H = 16.6 Hz, $=CH_\beta$), 5.82 (dd, 1H, ^3JH–H = 2.7 Hz, ^3JH–H = 5.5 Hz, $H^{3/4}$), 4.65 (dd, 1H, ^3JH–H = 3 Hz, ^3JH–H = 5 Hz, H^1), 4.56 (s, 3H, OMe), 3.81 (s, 3H, NMe*Z*), 3.57 (m, 1H, $H^{2/5}$), 3.40 (s, 3H, NMe*E*), 3.07 (m, 2H, $H^{2/5}$and H^6), 1.23 (m, 2H, CH_2). ^{13} C [^{1}H]-NMR (50.32 MHz, $CDCl_3$): $\delta = 334.8$ (W=*C*(O), 252.6 (W=*C*(N), 203.5, 203.2 (CO *trans*), 198.5, 197.4 (CO *cis*), 143.9 (C_6H_4), 139.1 ($C^{3/4}$), 138.3 (C_α), 132.8 ($C^{3/4}$), 127.9, 126.8 (C_6H_4), 123.5 (C_β), 81.9 (OMe), 70.2 (C^1), 53.6 (NMe*Z*), 50.5 (C^5), 49.9($C^{1/6}$), 48.9($C^{1/6}$), 47.9 (CH_2), 44.2 (NMe*E*). IR (CH_2Cl_2, cm^{-1}): 2068, 2061 (m, νCO), 1929 (s, νCO).

Selected data for **7**: (yield: 25%). ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 7.74$ (d, 1H, ^3JH–H = 15.8 Hz, $=CH_\alpha$), 7.58 (d, 2H, ^3JH–H = 8.3 Hz, C_6H_4), 7.47 (d, 2H, ^3JH–H = 8.1 Hz, C_6H_4), 7.15 (d, 1H, ^3JH–H = 16.3 Hz, $=CH_{\alpha'}$), 6.49 (d, 1H, ^3JH–H = 16.0 Hz, $=CH_\beta$), 6.01 (d, 1H, ^3JH–H = 16.0 Hz, $=CH_{\beta'}$), 3.91 (s, 3H, OMe), 3.87 (s, 3H, NMe*Z*), 3.50 (s, 3H, NMe*E*), ^{13} C[^{1}H]-NMR (50.32 MHz, $CDCl_3$): $\delta = 167.4$ (CO), 139.3 (C_α), 137.8 ($C_{\alpha'}$), 134.1, 128.3, 127.0 (C_6H_4), 122.3 (C_β), 118.9 ($C_{\beta'}$), 53.5 (NMe*Z*), 51.8 (OMe), 44.4 (NMe*E*). IR (KBr, cm^{-1}): 1710 (m, νC(O)OMe), 1630 (m, νC(O)NMe_2).

The structural assignment of **7** was made by an independent high yield (90%) synthesis, i.e. by stirring **2** in DMSO at room temperature (Scheme 3). This second example demonstrates again that the cycloaddition occurs exclusively at the methoxy–alkenylcarbene fragment. Thus, this preliminary study shows that it is possible to discriminate chemically two carbene groups within the same molecule.

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