# Formal [4+3], [4+2], [4+1] and [2+1] Cycloadditions and Acid–Base Reaction of 2-Methyl-1,3-dimorpholino-1,3-butadiene with Fischer Carbene Complexes

**José Barluenga,* Fernando Aznar and Mónica Fernández**

**Abstract:** 2-Methyl-1,3-dimorpholino-1,3-butadiene **1** reacted with $\alpha,\beta$-unsaturated Fischer carbene complexes to give a wide range of different products depending on the substitution pattern. Thus, seven-membered rings (**4**, **5** and **6**) could be obtained from chromium complexes **2** with aromatic or vinylic groups at the $\beta$ position. Similar results were observed when $\alpha$-methyl-substituted carbene complex **7a** was used. Six-membered carbocycles (derivatives of cycloadducts **12** and **13**) were isolated after reaction with both chromium and tungsten complexes bearing one or two alkyl groups at the $\beta$ position (**10** and **11**). Moreover, cyclopentenones **20** were the main products when the starting carbene complexes were alkyl-substituted at both $\alpha$ and $\beta$ positions (**19a,b**) or when aromatic (**19c,d**) instead of vinylic complexes were used. A bicyclo[4.1.0]heptene system **18** has also been obtained in the special case of reaction with $\beta,\beta$-dimethylvinylchromium complex **13b**; its formation could be explained as a formal carbene insertion into a C–H bond. The behaviour of diene **1** towards alkoxymethylcarbene complexes **22** was unusual. The different reaction products (cyclopentadienes **23**, bicyclo[3.1.0]hexenes **24**, aromatic amine **25** and metallatrienes **26**) imply a mechanism in which the deprotonation of the carbene complex by the diene is followed by Michael addition to the iminium salt formed.

**Keywords**
C–H activation · carbene complexes · cycloadditions · 1,3-diamino-1,3-butadiene

## Introduction

The utilization of Fischer carbene complexes in organic synthesis has been actively pursued since their discovery in 1964,[1] and they have found extensive use both in thermal reactions with alkenes to form cyclopropanes,[2] with alkynes to form quinone derivatives (Dötz benzannulation reaction),[3] and in photochemical reactions to produce ketene-derived products.[4]

However, few studies of the reactivity of Fischer carbene complexes with dienes have been carried out,[5] and the majority of work in the field of electron-rich dienes has utilized oxygenated dienes. The [4+2] cycloadditions of chromium and tungsten vinyloxy complexes, reported by Wulff, are characteristic reactions of this type of compound.[6] The same author communicated the first examples of cyclopropanations, formal [2+1] cycloadditions which give rise to vinylcyclopropanes. In one particular example, a seven-membered ring was formed, probably by a tandem cyclopropanation/Cope rearrangement process.[5f]

In the last few years our research group has been concerned with the scope and behaviour of 2-amino-1,3-butadienes as substrates for such reactions. These electron-rich dienes hold the decisive advantage that use of a chirally modified amine may promote diastereoselectivity in the cycloaddition step.[7] In preceding reports we described the reactivity of Fischer carbene complexes with the cited dienes to furnish seven-membered carbocycles[8] (through a formal [4+3] process), vinylaminocarbenes through a metathesis reaction[9] and [4+2] cycloadducts.[10]

Encouraged by these good results we decided to go one step further using even more activated dienes. Recently, we developed a synthesis of the new diene 2-methyl-1,3-dimorpholino-1,3-butadiene, diamino-substituted at 1 and 3 positions. Its preparation and a brief overview of its reactivity towards a selection of classical carbo- and heterodienophiles were reported.[11] We further investigated the reaction of this diene with a selection of Fischer-type complexes in order to study its reactivity with regard to the carbene complex structure. Herein we present the results obtained.

## Results and Discussion

We first examined the behaviour of chromium and tungsten alkenylmethoxycarbene complexes towards diene **1** in an attempt to establish whether the substitution pattern could play a role in the chemoselectivity of the reaction. With this idea in mind, we chose a set of complexes bearing different kinds and

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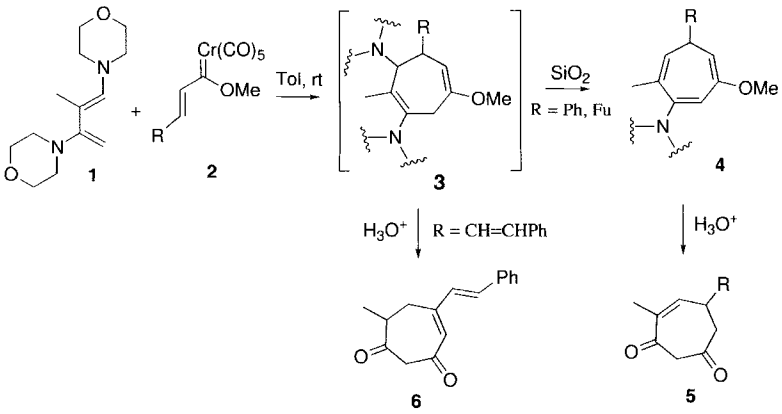
numbers of substituents at the α and β positions. We started with aryl or vinyl β-substituted vinylcarbene complexes **2**, which reacted smoothly with diene **1** at room temperature in toluene, leading to cycloheptadiene derivatives **3** in almost quantitative yields (Scheme 1). It had been proposed that these compounds




Scheme 1. [4 + 3] Cycloaddition of diene **1** to α,β-unsaturated chromium carbenes to obtain seven-membered rings.

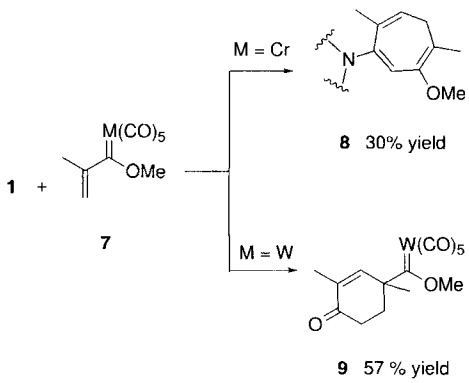
arise from cyclopropanation of the richer and less sterically hindered double bond of the diene and Cope rearrangement under the reaction conditions, although recent work has demonstrated that, with certain electron-rich dienes, the reaction is best explained by a nucleophilic attack of the diene at the carbene carbon of the complex, followed by 1,2 metal migration, cyclization and metal extrusion.[12] The structure of postulated adducts **3** was inferred from the $^1$H and $^{13}$C NMR analysis of the crude reaction product, in which only one diastereoisomer could be detected. Stereochemical assignment was not possible from this analysis, and attempted purification of **3** through a short silica gel column led to cycloheptatrienes **4** (Table 1). These compounds could be fully characterized except for **3c** (R = 2-phenylvinyl), treatment of which with silica gel afforded a mixture of products from isomerization of the unsaturated structure. Cycloheptatrienes **4** and adduct **3c** were hydrolyzed to the cycloheptadiones **5** and **6**, respectively, by treatment of their solutions in acetone with 3 N aqueous HCl at room temperature for 4 hours.

Next we turned our attention to alkenylmethoxycarbene complexes with alkyl substituents: isopropenyl complexes **7** were chosen as a model to investigate the effect in reactivity of an unsubstituted β position in the carbene complex. Diene **1** reacted with isopropenyl complexes **7** in toluene at room temperature, and it could be observed that the metal affected the product distribution. Thus, when the chromium carbene **7a** was used, only the seven-membered ring **8** could be isolated in 30% yield, while the [4 + 2] cycloadduct **9** was the main product when the tungsten complex **7b** was employed as the starting material (Scheme 2). This sensitivity to the nature of the metal in the chemoselectivity of the reaction has previously been observed.[5d]

Table 1. Synthesis of cycloheptatrienes **4** and cycloheptenediones **5** and **6**.

| Entry | R | Complex | Product | Yield (%) |
|---|---|---|---|---|
| 1 | 2-Furyl | **2a** | **4a** | 74 |
| 2 | Ph | **2b** | **4b** | 62 |
| 3 [a] | 2-Furyl | **2a** | **5a** | 82 |
| 4 [a] | Ph | **2b** | **5b** | 80 |
| 5 | (*E*)-CH=CHPh | **2c** | **6** | 71 |

[a] Yields from compounds **4**.




Scheme 2. Chemoselective reaction of diene **1** with pentacarbonyl[1-methoxy-2-methyl-2-propenylidene]tungsten(0) and -chromium(0).

After seeing these results we examined tungsten complexes **10** and chromium complexes **11**, with one[13] (**10a**, **11a**) or two (**10b**, **11b**) methyl substituents at the β position. They underwent [4 + 2] cycloaddition to diene **1** at room temperature, giving rise to the new carbenes **12** and **13** (Scheme 3). $^1$H NMR

**Abstract in Spanish:** *El 2-metil-1,3-dimorfolino-1,3-butadieno **1** reacciona con carbenos de Fischer α, β-insaturados para dar un amplio rango de productos diferentes dependiendo de su sustitución. Así, los ciclos de siete eslabones **4**, **5** y **6** se obtuvieron empleando los complejos de cromo **2**, con sustituyentes aromáticos o vinílicos en posición β. Se observaron resultados similares cuando se empleó el complejo **7a**, con un sustituyente metilo en posición α. Por otro lado los ciclos de seis eslabones, derivados de los cicloaductos **12** y **13**, se produjeron despues de la reacción con complejos de cromo y wolframio con sustituyentes alquilo en posición β(**10** y **11**). Además, las ciclopentenonas **20** fueron el principal producto de la reacción cuando el carbeno de partida tenía sustituyentes alquilo en posiciones α y β (**19a**, **b**) o cuando en vez de vinil carbenos se emplearon los complejos aromáticos **19**. También se obtuvo el biciclo[4.1.0]hepteno **18** en el caso de la reacción con el complejo de cromo β,β-dimetilvinil **13b**; su formación se podría explicar como una inserción formal en un enlace C–H. Se observó un comportamiento poco habitual cuando se hizo reaccionar el dieno **1** los con alcoximetil complejos **22**. Los diferentes productos de reacción (ciclopentadienos **23**, biciclo-[3.1.0]hexenos **24**, amina aromática **25** y metalatrienos **26**) apoyan un mecanismo en el que el dieno es capaz de abstraer uno de los protones en α del complejo carbeno y a continuación se produce una adición tipo Michael a la sal imonio que se forma.*



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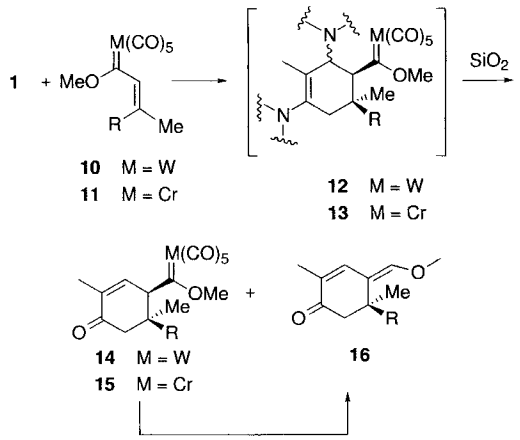



Scheme 3. [4+2] Cycloaddition of diene **1** to α,β-unsaturated carbene complexes alkyl-substituted in the β-position.

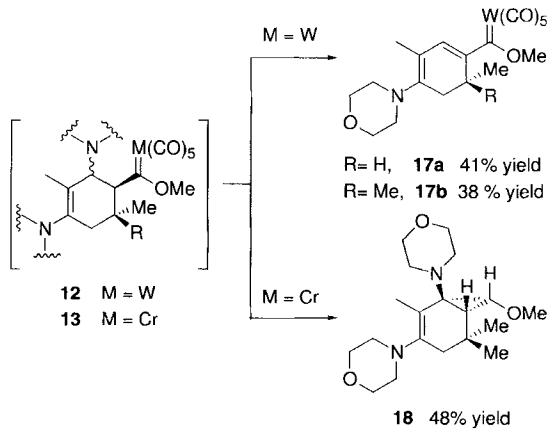
analysis of the crude reaction products revealed the presence of the cited cycloadducts as a mixture of two diastereoisomers in ratios ranging from 3:2 to 2:1. Further stereochemical assignments were not possible due to the instability of **12** and **13**, which afforded different products depending on the workup, as will now be detailed, but always with elimination of morpholine.

Thus, if the reaction products were filtered through a short silica gel column once TLC analysis had revealed the disappearance of the red starting alkeny complex (about half an hour), elimination of morpholine and enamine hydrolysis in the cycloadducts **12** and **13** led to carbene complexes **14** and **15**. The tungsten complex **14a** (R = H) could be isolated in 32% yield and fully characterized, even though it turned out to be quite unstable and decomposed to enol ether **16a**. The stereochemistry of **14a** was assigned based on $^1$H NMR spectroscopic data; the 11.2 Hz value of $^3J\,H_1-H_6$ clearly indicated a *trans* relationship between the methyl group and the carbene moiety. The chromium complexes, in contrast, are less stable and, consequently, NMR spectra of **15a** and **15b** were contaminated with variable amounts of **16a** and **16b**, respectively. The structure suggested for the complexes **15**, in which the double bond is not conjugated with the carbene–metal double bond, was supported by the observation in the $^1$H NMR spectrum of a singlet at $\delta = 1.8$ (**15a**) or 1.9 (**15b**) that was assigned to the methyl group at position 3 of the cycle. Compounds **16** were isolated as the main products by means of a longer silica gel column (see experimental section) and they were obtained as single isomers at the enol ether double bond (the structure was confirmed by NOE experiments) although, in solution at room temperature, slow isomerization to give the (*E*)/(*Z*) mixture could be observed. As can be seen in Table 2, the change of metal from chromium to tungsten resulted in an improved yield of the compound **16a**.

Table 2. Synthesis of methoxymethylenecyclohexenones **16**.

| Entry | Metal | R | Complex | Product | Yield (%) |
|---|---|---|---|---|---|
| 1 | W | H | **10a** | **16a** | 62 |
| 2 | Cr | H | **11a** | **16a** | 46 |
| 3 | Cr | Me | **11b** | **16b** | 48 |

In a separate series of experiments the reactions were not quenched immediately after the disappearance of the starting material. In these cases new products, arising from evolution of complexes **12** and **13**, could be isolated. Thus, longer reaction times in solution at room temperature of tungsten carbenes **12** led to a progressive change from dark yellow to deep violet solutions as a consequence of formation of the metallatrienes **17** through morpholine elimination in the reaction conditions (Scheme 4). Complexes **17** could be isolated from the reaction




Scheme 4. Differing evolution of the [4+2] cycloadducts **12** and **13** depending on the metal.

media as dark violet crystals. Not unexpectedly, the reaction of **1** with the more bulky carbene **10b** proceeded more sluggishly, and consequently, the cycloaddition rate was similar to morpholine elimination and the only reaction product was metallatriene **17b**.

In contrast with this behaviour, while no evolution was observed for the chromium cycloadduct **13a** under the same conditions as described above, the complex **13b** was, surprisingly, stereospecifically transformed into a new bicyclo[4.1.0]heptene **18**, which could be isolated as the main reaction product. The formation of this structure can be described as a formal carbene insertion into C–H bond and metal elimination in **13b**. The yield was optimized and the best result was obtained in toluene at 110 °C with a 3-to-1 excess of the starting complex; otherwise slow decomposition of vinylidene complex **11a** in the reaction conditions prevented the total consumption of diene **1**. While C–H insertion processes are commonly observed in reactions involving metal carbenoids,[14] they are rare for isolable transition metal carbene complexes[15] and the yields are synthetically useful only when non-heteroatom-stabilized metal carbene complexes are the active species, otherwise insertion compounds are isolated in very low yields as side products in cyclopropanation reactions of electron-deficient olefins and dienes.[5h, j] However, it has been reported that boroxy Fischer complexes undergo efficient intramolecular C–H insertion.[16]

The cyclohexenylmethoxycarbene **19a** and the cyclopentenylmethoxycarbene **19b** were chosen as examples of substitution at both α and β positions. Surprisingly, a different mode of reactivity was observed for these complexes, and the formal [4+1] adducts **20** (Scheme 5)[17] were obtained in good yield (entries 1 and 2, Table 3) under similar conditions to those used in previ-

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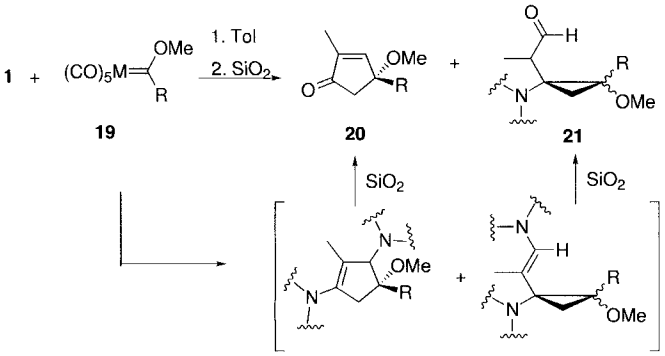


Scheme 5. [4+1] Cycloaddition and cyclopropanation reactions of diene **1** with cycloalkenylcarbene complexes.

Table 3. Synthesis of cyclopentenones **20** and cyclopropanes **21**.

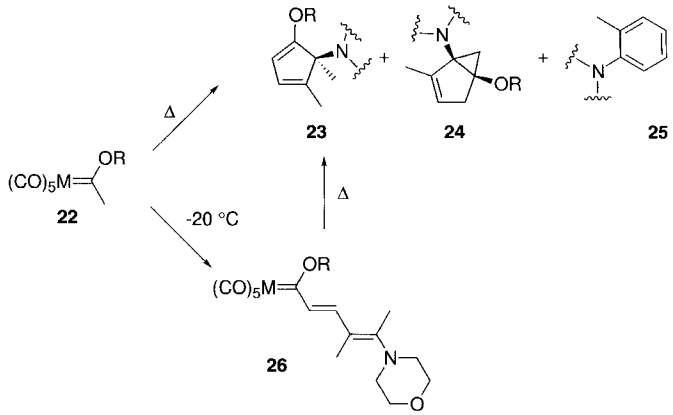
| Entry | M | R | **20** (%) | *trans*-**21**(%) | *cis*-**21**(%) |
|---|---|---|---|---|---|
| 1 | Cr |  | 54 | – | – |
| 2 | Cr |  | 63 | – | – |
| 3 | Cr | Ph | 25 | 7 | 6 |
| 4 | Mo | Ph | 24 | 11 | 9 |

ous reactions (room temperature and toluene as solvent). This result contrasts with the behaviour of similar activated dienes toward this kind of carbene complexes; thus, Danishefsky's diene was reported to react with complex **19a** (R = cyclohexenyl) in benzene at room temperature to give rise to a mixture of seven-membered carbocycle and *trans*-divinylcyclopropane;[5d] similar results were obtained when 2-amino-1,3-butadienes alkyl-substituted at C4 were used, although heating at 60 °C (THF, 3 h) was required.[8b]

To the best of our knowledge only one similar example has previously appeared in the literature, namely the five-membered ring formed upon reaction of electron-deficient diene methyl sorbate with pentacarbonyl[(*N*,*N*-dimethylamino)methylene]-chromium.[5k] Small amounts of cyclopentene derivatives were detected in cyclopropanation reactions of electron-deficient dienes, but they may result from thermal rearrangement of vinyl cyclopropanes due to the long reaction time and not from a direct [4+1] cycloaddition.[5j]

In order to examine the role of the double bond of the cycloalkenyl moiety in the [4+1] cycloaddition, we decided to treat diene **1** with a Fischer complex substituted with an aromatic system. The reaction of chromium complex **19c** with diene **1** under standard conditions (toluene as solvent at room temperature) was very slow, and the only isolable products were pentacarbonylmorpholinochromium(0) and pentacarbonyl[(1-morpholino-1-phenyl)methylene]chromium(0) complexes. However, when heated for 1 h in toluene at 110 °C the [4+1] cycloadduct **20c** could be isolated as main reaction product along with small amounts of cyclopropanation products **21** (Scheme 5).[18] It is known that the metal plays an important role in the reactivity of these complexes; the mildest reaction conditions have been reported for carbenes containing molybdenum.[19] As expected, less harsh conditions were required when the molybdenum complex (**19d**) was used, and the starting complex was consumed in 12 h at room temperature or in half an hour at 60 °C (see Table 3).

A completely different type of behaviour was observed in the reaction of methylchromium carbenes **22**, which have acidic α-hydrogens, with diene **1**. Deprotonation by the diene acting as base was the main reaction pathway. When the reactants were mixed together in toluene (Scheme 6), the solution turned deep violet, indicating the new reaction pattern. This deeply coloured product could not be purified by silica gel chromatography as it decomposed in the reaction medium at room temperature into a mixture of unidentifiable products. However, when the reaction mixture was refluxed in toluene or THF, easily separable mixtures of products **23**, **24** and **25** were obtained. Yields were



Scheme 6. Reaction of diene **1** with methylalkoxycarbene complexes.

higher in toluene (110 °C) than in THF (64 °C) (see Table 4, entries 1 and 3) and no cyclopropanation product **24** was observed when a bulky *tert*-butyl group was attached to the oxygen in the carbene complex (Table 4, entry 6).

Table 4. Synthesis of compounds **23**, **24** and **25**.

| Entry | M | Solvent | OR | **23** (%) | **24** (%) | **25** (%) |
|---|---|---|---|---|---|---|
| 1 | Cr | THF | OMe | 10 | 8 | 20 |
| 2 | Cr | THF | OBn | 14 | 9 | 14 |
| 3 | Cr | toluene | OMe | 24 | 23 | – |
| 4 | W | toluene | OMe | 22 | 20 | 17 |
| 5 | Cr | toluene | OBn | 23 | 15 | 10 |
| 6 | Cr | toluene | O*t*Bu | 31 | – | – |

The reaction was monitored by NMR analysis at room temperature, with [$D_6$]benzene as solvent. The formation of a new complex could be observed. The complex reached its highest concentration after 2 h; from this time on decomposition was observed. This carbene complex was identified as **26**, and could be obtained in very good yield (Table 5) by allowing the reaction

Table 5. Synthesis of metallatrienes **26** and cyclopentadienes **23**, and **24**.

| Entry | Complex | M | OR | Yield (%) | **23** (%) | **24** (%) |
|---|---|---|---|---|---|---|
| 1 | **26a** | Cr | OMe | 92 | 74 | – |
| 2 | **26b** | Cr | OBn | 98 | 90 | – |
| 3 | **26c** | Cr | O*t*Bu | 73 | 54 | – |
| 4 | **26d** | W | OMe | 95 | 70 | 8 |



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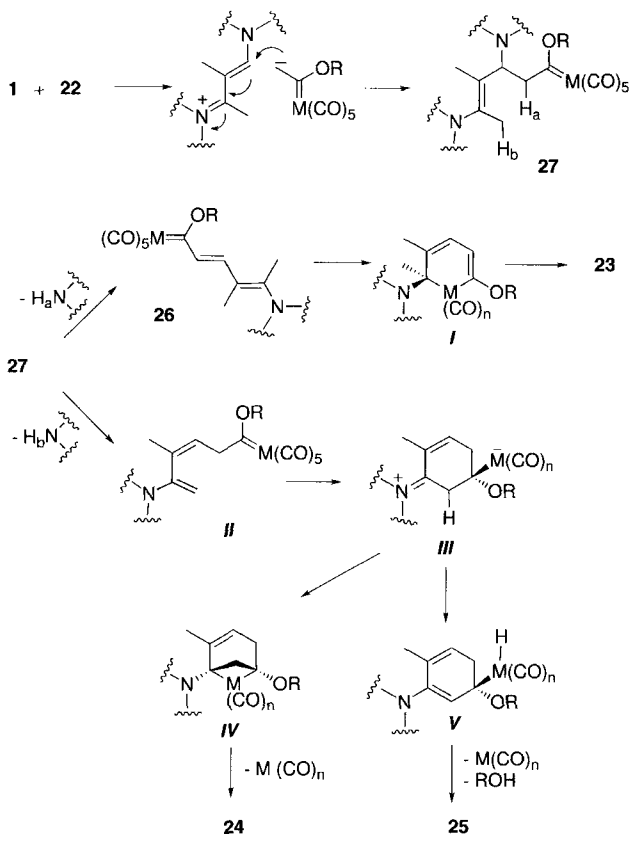
to progress for 2 h at room temperature and then at −20 °C overnight. Once the violet compounds were isolated by crystallization from the reaction media, they were dissolved in toluene and heated to 110 °C, giving rise exclusively to products **23** in good yields.[20]

A plausible mechanism accounting for the formation of **23**, **24** and **25** as well as carbene complex **26** involves an acid–base reaction as the first step, followed by a Michael-type addition of the anionic species to the $\alpha,\beta$-unsaturated iminium salt (Scheme 7) resulting in the formation of intermediate carbene




Scheme 7. Proposed mechanism for the reaction of diene **1** with methylalkoxycarbene complexes.

complex **27**. This intermediate would subsequently undergo morpholine elimination to give 1-metalla-1,4,6-hexatriene ***II*** or 1-metalla-1,3,5-hexatriene **26**. At low temperature complex **26** was isolated from the reaction medium as dark violet crystals and heating was required to promote double-bond isomerization to the (*Z*) configured species, this being a geometric prerequisite for its cyclization to cyclopentadiene **23**,[20a] probably through metallacyclohexadiene ***I***. On the other hand, when starting carbene complex **22** and diene **1** were heated together two different reaction paths operated with both the conjugated **26** and the nonconjugated ***II*** metallatriene species being formed from intermediate **27**. It seems that, once formed, conjugated 1,3,5-metallatriene **26** reacts rapidly to produce the cyclopentadiene, as previously described, whereas the nonconjugated 1,4,6-metallatriene ***II*** could undergo enamine attack to the carbene moiety to generate intermediate ***III***;[21] this species could undergo rapid decomplexation either via metallabutane ***IV*** to give the cyclopropanation product **24** or via intermediate ***V***, which after reductive elimination and loss of alcohol would give aromatic amine **25**.

## Conclusion

In summary, 2-methyl-1,3-dimorpholino-1,3-butadiene has proved to be an interesting reagent in reactions with Fischer carbene complexes: first of all, the wide range of products obtained is noteworthy, comprising different-sized metal-free carbocycles as well as new Fischer carbene complexes difficult to prepare by other methods, which have been isolated in yields ranging from moderate to good. The metal and the substituents in the carbene complex have been observed to play an important role in the reaction chemoselectivity; not only alkyl, aryl or vinyl carbene complexes but, in the special case of vinyl complexes, the type, position and quantity of the substituents attached to the double bond, have determined the reaction pattern. Moreover, there is a wide variety of reaction pathways, some of which have not been previously observed with other electron-rich dienes.

## Experimental Section

**General Considerations:** Tetrahydrofuran (THF) and toluene were distilled from benzophenone ketyl under nitrogen prior to use. Chromatographic purifications were performed on silica gel 60, 230–400 mesh. TLC was performed on glass-backed plates coated with silica gel $60F_{254}$ and, unless otherwise specified, $R_f$ of the products is given in hexane/EtOAc 3:1. Components were located by treating the plates with an acidic solution of Mo(VI) and Ce(IV) salt complexes and heating. Chromatographic solvents were distilled prior to use. NMR measurements were recorded on Bruker AC-200 or AC-300 spectrometers. IR analysis was performed with a Mattson 3000 FTIR spectrometer. Electron impact (EI) mass spectra were determined on a Finnigan Mat95 Mass Spectrometer. Elemental analyses were carried out with a Perkin–Elmer 240 B microanalyzer.

2-Methyl-1,3-Dimorpholino-1,3-Butadiene **1** was prepared according to the published procedure[11] and carbene complexes were prepared by the standard method.[22]

**General Procedure for the Synthesis of Cycloheptatrienes 4 and 8:** Diene **1** (1 mmol) was added to a solution of a Fischer carbene complex **2** or **7a** (1 mmol) in dry toluene (2 mL) at room temperature. The reaction mixture was stirred at room temperature overnight and concentrated at reduced pressure ($10^{-2}$ Torr). The crude product was dissolved in dry hexane and filtered through a pad of Celite. The clear solution was concentrated at reduced pressure (water aspirator) and then filtered through a short silica gel column with hexane and ethyl acetate (3:1) as eluent.

**7-(2-Furyl)-5-methoxy-2-methyl-3-(*N*-morpholino)-1,3,5-cycloheptatriene (4a):** Pentacarbonyl[1-methoxy-*trans*-3-(2-furyl)-2-propenylidene]chromium(0) (**2a**, 1 mmol, 328 mg) was treated with 2-methyl-1,3-dimorpholino-1,3-butadiene (**1**, 1 mmol, 238 mg) in toluene for 16 h to yield 212 mg (74%) of **4a**. $R_f$ = 0.67; $^1$H NMR (200 MHz, $CDCl_3$, RT, $CHCl_3$): $\delta$ = 1.90 (s, 3H; $CH_3$), 2.72–2.98 (m, 4H; morpholine), 3.21 (dd, $^3J$(H,H) = 5.4 Hz, $^3J$(H,H) = 7.0 Hz, 1H; CHAr), 3.52 (s, 3H; $CH_3O$), 3.65–3.85 (m, 4H; morpholine), 4.72 [d, $^3J$(H,H) = 5.4 Hz, 1H; CH=C(OMe)], 5.64 [s, 1H; CH=C(morpholine)], 5.76 [d, $^3J$(H,H) = 7.0 Hz, 1H; CH=C(Me)], 6.20 (dd, $^3J$(H,H) = 3.2 Hz, $^4J$(H,H) = 0.6 Hz, 1H; 2-furyl), 6.36 (dd, $^3J$(H,H) = 3.2 Hz, $^3J$(H,H) = 1.9 Hz, 1H; 2-furyl), 7.38 (dd, $^3J$(H,H) = 1.9 Hz, $^4J$(H,H) = 0.6 Hz, 1H; 2-furyl); $^{13}$C NMR (50.3 MHz, $CDCl_3$, RT, $CDCl_3$): $\delta$ = 20.3 ($CH_3$), 35.8 (CHAr), 50.5 ($CH_2$, morpholine) 55.4 ($CH_3O$), 66.7 ($CH_2$, morpholine), 96.8 [*C*H=C(OMe)], 104.3 [*C*H=C(morpholine)], 105.0 (2-furyl), 110.0 (2-furyl), 128.6 (CH=), 128.8 [(Me)C=], 141.1 (2-furyl), 155.3 (2-furyl), 155.6 [(MeO)C=], 156.9 [(morpholine)C=]; HREIMS calcd for $C_{17}H_{21}NO_3$ 287.152132, found 287.151596.

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**5-Methoxy-2-methyl-3-morpholino-7-phenyl-1,3,5-cycloheptatriene (4b)**: Compound **2a** (1 mmol, 338 mg) was treated with **1** (1 mmol, 238 mg) in toluene for 16 h to yield 0.184 (62%) of **4b**. $R_f = 0.65$; $^1$H NMR (200 MHz, $CDCl_3$, RT, $CHCl_3$): $\delta = 1.97$ (s, 3H; $CH_3$), 2.75–3.10 (m, 4H; morpholine), 3.15 (dd, $^3J(H,H) = 5.4$ Hz, $^3J(H,H) = 6.7$ Hz, 1H; CHAr), 3.57 (s, 3H; $CH_3O$), 3.70–4.00 (m, 4H; morpholine), 4.73 [d, $^3J(H,H) = 5.4$ Hz, 1H; CH=C(OMe)], 5.74 [s, 1H; CH=C(morpholine)], 5.80 [d, $^3J(H,H) = 6.7$ Hz, 1H; CH=C(OMe)], 7.44 (m, 5H; Ph); $^{13}$C NMR (50.3 MHz, $CDCl_3$, RT, $CDCl_3$): $\delta = 20.2$ ($CH_3$), 41.8 (CHAr), 50.3 ($CH_2$, morpholine), 55.1 ($CH_3O$), 66.4 ($CH_2$, morpholine), 99.9 [*C*H=C(OMe)], 104.9 [*C*H=C(morpholine)], 126.0 (Ph), 127.2 (Ph), 127.7 (CH=), 128.2 (Ph), 131.7 [(Me)C=], 144.3 (Ph), 154.7 [(MeO)C=], 155.4 [(morpholine)C=]; HREIMS calcd for $C_{19}H_{23}NO_2$ 297.172867, found 297.173755.

**2-Methoxy-1,5-dimethyl-4-morpholino-1,3,5-cycloheptatriene (8)**: Pentacarbonyl[1-methoxy-2-methyl-2-propenylidene]chromium(0) (1 mmol, 276 mg) **7a** was treated with **1** (1 mmol, 238 mg) in toluene for 16 h to yield 70 mg (30%) of **8**; $R_f = 0.54$; $^1$H NMR (200 MHz, $CDCl_3$, RT, $CHCl_3$): $\delta = 1.84$ (s, 6H; $CH_3$), 2.11 (m, 2H; $CH_2$), 2.78 (m, 4H; morpholine), 3.47 (s, 3H; $CH_3O$), 3.77 (m, 4H; morpholine), 5.54 [s, 1H; CH=C(morpholine)], 5.57 [t, $^3J(H,H) = 7.8$ Hz, 1H; *C*H=C(Me)]; $^{13}$C NMR (50.3 MHz, $CDCl_3$, RT, $CDCl_3$): $\delta = 16.6$ ($CH_3$), 20.2 ($CH_3$), 31.4 ($CH_2$), 50.8 ($CH_2$, morpholine), 59.0 ($CH_3O$), 66.8 ($CH_2$, morpholine), 105.4 [*C*H=C(morpholine)], 115.3 [=*C*(Me)$CH_2$], 125.1 [CH=C(Me)], 130.1 [CH=*C*(Me)], 149.2 [(MeO)C=], 154.7 [(morpholine)C=]; HREIMS calcd for $C_{14}H_{21}NO_2$ 235.157218, found 235.156847.

**General Procedure for the Synthesis of 4-Cycloheptene-1,3-diones (5)**: Aqueous 3N HCl (0.5 mL) was added to a solution of cycloheptatriene **4** (0.5 mmol) in acetone (4 mL). The reaction mixture was stirred at room temperature for 4 h and extracted with diethyl ether (3 × 15 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (2 × 15 mL) and brine (15 mL), dried over $Na_2SO_4$ and evaporated. The crude product was chromatographed on silica gel with a mixture of hexane/ethyl acetate (3:1).

**6-(2-Furyl)-4-methyl-4-cycloheptene-1,3-dione (5a)**: Yield 82% (84 mg). $R_f = 0.33$; $^1$H NMR (200 MHz, $CDCl_3$, RT, $CHCl_3$): $\delta = 1.91$ (s, 3H; $CH_3$), 2.80–3.10 (m, 2H; $CH_2CO$), 3.75 (d, $^2J(H,H) = 13.8$ Hz, 1H; $COCH_2CO$), 4.13 (d, $^2J(H,H) = 13.8$ Hz, 1H; $COCH_2CO$), 4.39 (m, 1H; CHAr), 6.17 (dd, $^4J(H,H) = 0.6$ Hz, $^3J(H,H) = 3.2$ Hz, 1H; furyl), 6.35 (dd, $^3J(H,H) = 3.2$ Hz, $^3J(H,H) = 1.9$ Hz, 1H; furyl), 6.82 (d, $^3J(H,H) = 5.4$ Hz, 1H; CH=), 7.40 (dd, $^4J(H,H) = 0.6$ Hz, $^3J(H,H) = 1.9$ Hz, 1H; furyl); $^{13}$C NMR (50.3 MHz, $CDCl_3$, RT, $CDCl_3$): $\delta = 19.3$ ($CH_3$), 35.1 (CHAr), 45.2 ($CH_2CO$), 61.2 ($COCH_2CO$), 105.7 (furyl), 110.4 (furyl), 138.6 [(Me)C=], 142.3 (furyl), 142.8 (CH=), 153.7 (furyl), 191.9 (=C(Me)*C*O), 201.6 (CO); HREIMS calcd for $C_{12}H_{12}O_3$ 204.078637, found 204.078884.

**4-Methyl-6-phenyl-4-cycloheptene-1,3-dione (5b)**: Yield 80% (85 mg). $R_f = 0.34$ ($SiO_2$, hexane/EtOAc 3:1); $^1$H NMR (200 MHz, $CDCl_3$, RT, $CHCl_3$): $\delta = 1.90$ (s, 3H; $CH_3$), 2.75–3.05 (m, 2H; $CH_2CO$), 3.69 (d, $^2J(H,H) = 14.0$ Hz, 1H; $COCH_2CO$), 4.26 (d, $^2J(H,H) = 14.0$ Hz, 1H; $COCH_2CO$), 4.30 (m, 1H; CHAr), 6.79 (d, $^3J(H,H) = 4.5$ Hz, 1H; CH=), 7.22–7.51 (m, 5H); $^{13}$C NMR (50.3 MHz, $CDCl_3$, RT, $CDCl_3$): $\delta = 19.4$ ($CH_3$), 41.6 (CHAr), 48.6 ($CH_2CO$), 61.2 ($COCH_2CO$), 127.0 (Ph), 127.3 (Ph), 129.1 (Ph), 138.2 [(Me)C=], 142.5 (Ph), 146.9 (CH=), 192.3 (=C(Me)CO), 202.2 (CO); HREIMS calcd for $C_{14}H_{14}O_2$ 214.099372, found 214.099741.

**5-(2-Phenylethenyl)-7-methyl-4-cycloheptene-1,3-dione (6)**: *Diene* **1** (1 mmol) was added to a solution of Fischer carbene complex **2c** (364 mg, 1 mmol) in dry toluene (2 mL) at room temperature. The reaction mixture was stirred at room temperature overnight and concentrated at reduced pressure ($10^{-2}$ Torr.). The crude product was dissolved in dry hexane and filtered through a pad of Celite. The clear solution was concentrated at reduced pressure (water aspirator), then redissolved in 4 mL of acetone and HCl (3N), stirred for 4 h and worked up as described above to yield 170 mg (71%). $R_f = 0.22$; $^1$H NMR (300 MHz, $CDCl_3$, RT, $CHCl_3$): $\delta = 1.26$ (d, $^3J(H,H) = 6.9$ Hz, 3H; $CH_3$), 2.73 (tdd, $^3J(H,H) = 6.9$ Hz, $^3J(H,H) = 8.6$ Hz, $^3J(H,H) = 3.4$ Hz, 1H; CHMe), 2.95 (dd, $^3J(H,H) = 8.6$ Hz, $^2J(H,H) = 15.9$ Hz, 1H; C*H*$_2$CHMe), 3.14 (dd, $^3J(H,H) = 3.4$ Hz, $^2J(H,H) = 15.9$ Hz, 1H; C*H*$_2$CHMe), 3.89 (d, $^2J(H,H) = 14.2$ Hz, 1H; $COCH_2CO$), 3.99 (d, $^2J(H,H) = 14.2$ Hz, 1H; $COCH_2CO$), 6.21 (s, 1H; =CHCO), 6.88 (d, $^3J(H,H) = 16.3$ Hz, 1H; C*H*=CHPh), 7.08 (d, $^3J(H,H) = 16.3$ Hz, 1H; CH=C*H*Ph), 7.3–7.6 (m, 5H; Ph); $^{13}$C NMR (75 MHz, $CDCl_3$, RT, $CDCl_3$): $\delta = 16.6$ ($CH_3$), 31.1 ($CH_2CHMe$), 44.4 (CHMe), 59.3 ($COCH_2CO$), 127.3 (Ph), 128.9 (Ph), 129.4 (Ph), 130.7 (*C*H=CHPh), 131.3 (*C*HCO), 135.4 (=CHPh), 135.5 (Ph), 153.9 (*C*=CHCO), 191.3 (=C*H*CO), 205.5 (CO); HREIMS calcd for $C_{16}H_{16}O_2$ 240.115021, found 240.115329.

**General Procedure for the Synthesis of Complexes 9 and 14a and 4-Methoxymethylenecyclohexenones (16)**: Diene **1** (1 mmol) was added to a solution of the Fischer carbene complex **7b**, **10** or **11** (1 mmol) in dry THF (5 mL) at room temperature. The reaction was stirred at this temperature for the time indicated and concentrated at reduced pressure ($10^{-2}$ Torr). The residue was chromatographed in silica gel with hexane/ethyl acetate (3:1).

**Pentacarbonyl[1,3-dimethyl-4-oxo-2-cyclohexenyl]methoxymethylene-tungsten(0) (9)**: Pentacarbonyl[1-methoxy-2-methyl-2-propenylidene]-tungsten(0) (**7b**, 1 mmol, 408 mg) was treated with diene **1** (1 mmol, 238 mg) in THF for 1 h to yield 279 mg (57%) of **9**. $R_f = 0.39$ ($SiO_2$, hexane/EtOAc 3:1); $^1$H NMR (200 MHz, $CDCl_3$, RT, $CHCl_3$): $\delta = 1.25$ (s, 3H; $CH_3C$), 1.90 [s, 3H; $(CH_3)C$=], 2.18–2.60 (m, 4H; C$H_2$C$H_2$), 4.75 (s, 3H; $CH_3O$), 7.07 (s, 1H; CH=); $^{13}$C NMR (50.3 MHz, $CDCl_3$, RT, $CDCl_3$): $\delta = 16.2$ (*C*$H_3$C), 24.6 [(*C*$H_3$)C=], 33.7 ($CH_2$), 34.9 ($CH_2$), 63.5 ($CH_3C$), 70.9 ($CH_3O$), 134.5 [(Me)C=], 150.4 (CH=), 197.0 (WCO), 198.5 (CO), 201.5 (WCO), 341.8 (W=C); IR ($CH_2Cl_2$, $cm^{-1}$): $\tilde{\nu} = 2070$, 1938; HREIMS calcd for $C_{15}H_{14}O_7W$ 490.022843, found 490.024221.

**Pentacarbonyl[*trans*-3,6-dimethyl-4-oxo-2-cyclohexenyl]methoxymethylene-tungsten(0) (14a)**: Pentacarbonyl[1-methoxy-*trans*-2-butenylidene]tungsten(0) **10a** (1 mmol, 408 mg) was treated with diene **1** (1 mmol, 238 mg) in THF for 1 h and chromatographed on a 25 × 2 cm silica gel column to yield 157 mg (32%). $R_f = 0.55$; $^1$H NMR (300 MHz, $CDCl_3$, RT, $CHCl_3$): $\delta = 1.04$ (d, $^3J(H,H) = 6.4$ Hz, 3H; C$H_3$CH), 1.23 (tddd, $^3J(H,H) = 6.4$ Hz, $^3J(H,H) = 12.9$ Hz, $^3J(H,H) = 11.2$ Hz, $^3J(H,H) = 3.4$ Hz, 1H; $CH_3CH$), 1.77 [s, 3H; $(CH_3)C$=], 2.17 (dd, $^2J(H,H) = 16.8$ Hz, $^3J(H,H) = 12.9$ Hz, 1H; $CH_2$), 2.43 (dd, $^2J(H,H) = 16.8$ Hz, $^3J(H,H) = 3.4$ Hz, 1H; $CH_2$), 4.63 (s, 3H; $CH_3O$), 4.62 (dd, $^3J(H,H) = 11.2$ Hz, $^3J(H,H) = 2.6$ Hz, 1H; C*H*CH=), 6.30 (d, $^3J(H,H) = 2.6$ Hz, 1H; CHC*H*=); $^{13}$C NMR (75 MHz, $CDCl_3$, RT, $CDCl_3$): $\delta = 15.6$ (*C*$H_3$CH), 19.8 (*C*$H_3$C=), 34.6 ($CH_3CH$), 45.0 ($CH_2$), 70.7 ($CH_3O$), 75.9 (*C*HCH=), 135.5 [(Me)C=], 139.6 (CH=), 196.7 (WCO), 198.5 (CO), 202.6 (WCO), 337.6 (W=C); IR ($CH_2Cl_2$, $cm^{-1}$): $\tilde{\nu} = 2073$, 1950; HREIMS calcd for $C_{15}H_{14}O_7W$ 490.022843, found 490.023410.

**2,5-Dimethyl-4-methoxymethylene-2-cyclohexenone (16a)**:

**Method A**: Pentacarbonyl[1-methoxy-*trans*-2-butenylidene]chromium(0) (**11a**, 1 mmol, 276 mg) was treated with diene **1** (1 mmol, 238 mg) in THF for 3 h to yield 76 mg (46%) of **16a**.

**Method B**: Compound **10a** (1 mmol, 408 mg) was treated with diene **1** (1 mmol, 238 mg) in THF for 1 h to yield 103 mg (62%) of **16a**. $R_f = 0.34$ ($SiO_2$, hexane/EtOAc 3:1); $^1$H NMR (200 MHz, $CDCl_3$, RT, $CHCl_3$): $\delta = 1.04$ (d, $^3J(H,H) = 7.0$ Hz, 3H; $CH_3$), 1.80 (s, 3H; $CH_3C$=), 2.28 (dd, $^2J(H,H) = 15.9$ Hz, $^3J(H,H) = 1.8$ Hz, 1H; $CH_2$), 2.59 (dd, $^2J(H,H) = 15.9$ Hz, $^3J(H,H) = 6.7$ Hz, 1H; $CH_2$), 3.19 (tdd, $^3J(H,H) = 7.0$ Hz, $^3J(H,H) = 6.7$ Hz, $^3J(H,H) = 1.8$ Hz, 1H; C*H*Me), 3.75 (s, 3H; $CH_3O$), 6.33 [s, 1H; (Me)C=C*H*], 6.62 [s, 1H; (MeO)CH=]; $^{13}$C NMR (50.3 MHz, $CDCl_3$, RT, $CDCl_3$): $\delta = 15.5$ (*C*$H_3$CH), 19.6 (*C*$H_3$C=), 27.4 (MeCH), 43.6 ($CH_2$), 60.6 ($CH_3O$), 119.9 (C=), 129.1 (C=), 140.7 [*C*H=C(Me)], 150.0 [(MeO)CH=], 199.2 (CO); HREIMS calcd for $C_{10}H_{14}O_2$ 166.099372, found 166.099413.

**2,5,5-Trimethyl-4-methoxymethylene-2-cyclohexenone (16b)**: Pentacarbonyl[1-methoxy-3-methyl-2-butenylidene]chromium(0) **11b** (1 mmol, 290 mg) was treated with diene **1** (1.5 mmol, 357 mg) in THF for 48 h to yield 86 mg (48%). $R_f = 0.46$ ($SiO_2$, hexane/EtOAc 3:1); $^1$H NMR (300 MHz, $CDCl_3$, RT, $CHCl_3$): $\delta = 1.25$ [s, 6H; $(CH_3)_2C$], 1.82 (s, 3H; $CH_3C$=), 2.30 (s, 2H; $CH_2$), 3.74 (s, 3H; $CH_3O$), 6.37 [s, 1H; (Me)C=CH], 6.53 [s, 1H; (MeO)CH=]; $^{13}$C NMR (75 MHz, $CDCl_3$, RT, $CDCl_3$): $\delta = 15.2$ [$(CH_3)_2C$], 27.5 [$(CH_3)_2C$], 35.5 [$(CH_3)_2C$], 52.6 ($CH_2$), 61.0 ($CH_3O$), 122.2 (C=), 128.1 (C=), 143.6 [(Me)CH=], 152.6 [(MeO)CH=], 199.0 (CO); HREIMS calcd for $C_{11}H_{16}O_2$ 180.115022, found 180.114532.

**General Procedure for the Synthesis of Metallatrienes 17**: Diene **1** (1 mmol) was added to a solution of the complex **10** (1 mmol) in dry THF (5 mL) at room temperature. The reaction was stirred at room temperature for the time



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indicated and concentrated at reduced pressure ($10^{-2}$ Torr). Then dry $CH_2Cl_2$ (1 ml) and dry hexane (7 mL) were added and the reaction mixture cooled down (−20 °C) till dark crystals were obtained. The solvents were decanted off through a cannula and the crystals dried under high vacuum.

**Pentacarbonyl[3,6-dimethyl-4-morpholino-1,4-cyclohexadienyl]methoxymethylenetungsten(0) (17a)**: Compound **10a** (1 mmol, 408 mg) was treated with diene **1** (1 mmol, 238 mg) in THF for 4 h to yield 229 mg (41%). $^1$H NMR (300 MHz, $CDCl_3$, RT, $CHCl_3$): $\delta = 0.88$ (d, $^3J$(H,H) = 6.9 Hz, 3H; $CH_3$), 2.00 (s, 3H; $CH_3C$=), 2.13 (dd, $^2J$(H,H) = 15.0 Hz, $^3J$(H,H) = 1.7 Hz, 1H; $CH_2$), 2.47 (dd, $^2J$(H,H) = 15.0 Hz, $^3J$(H,H) = 8.2 Hz, 1H; $CH_2$), 3.16 (tdd, $^3J$(H,H) = 6.9 Hz, $^3J$(H,H) = 8.2 Hz, $^3J$(H,H) = 1.7 Hz, 1H; CHMe), 3.29–3.42 (m, 2H; morpholine), 3.49–3.60 (m, 2H; morpholine), 3.70–3.83 (m, 4H; morpholine), 4.43 (s, 3H; $CH_3O$), 7.73 (s, 1H; CH=); $^{13}$C NMR (75 MHz, $CDCl_3$, RT, $CDCl_3$): $\delta = 17.3$ ($CH_3CH$), 20.7 ($CH_3C$=), 28.1 (MeCH), 34.3 ($CH_2$), 49.8 ($CH_2$, morpholine), 67.1 ($CH_3O$), 67.4 ($CH_2$, morpholine), 107.9 [(Me)C=], 144.4 (C=CH), 159.9 [(morpholine)C=], 164.3 (CH=), 199.3 (WCO), 203.2 (WCO), 282.0 (W=C); IR ($CH_2Cl_2$, cm$^{-1}$): $\tilde{\nu}$ = 2056, 1921; $C_{19}H_{21}NO_7W$ (559.23): calcd C 40.81, H 3.79, N 2.50; found C 40.56, H 3.58, N 2.39.

**Pentacarbonyl[3,6,6-trimethyl-4-morpholino-1,4-cyclohexadienyl]methoxymethylenetungsten(0) (17b)**: Pentacarbonyl[1-methoxy-3-methyl-2-butenylidene]tungsten(0) (**10b**, 1 mmol, 422 mg) was treated with diene **1** (1 mmol, 238 mg) in THF for 8 h to yield 218 mg (38%) of **17b**. $^1$H NMR (200 MHz, $CDCl_3$, RT, $CHCl_3$): $\delta = 1.13$ [s, 6H; $(CH_3)_2C$], 1.92 (s, 3H; $CH_3C$=), 2.18 (s, 2H; $CH_2$), 3.31 (m, 4H; morpholine), 3.72 (m, 4H; morpholine), 4.49 (s, 3H; $CH_3O$), 7.42 (s, 1H; CH=); $^{13}$C NMR (50.3 MHz, $CDCl_3$, RT, $CDCl_3$): $\delta = 19.4$ ($CH_3C$=), 25.6 [$(CH_3)_2C$], 39.7 ($CH_2$), 44.2 [$(CH_3)_2C$], 49.6 ($CH_2$, morpholine), 67.2 ($CH_3O$), 67.4 ($CH_2$, morpholine), 108.7 ((Me)C=), 151.5 (C=CH), 155.9 [(morpholine)C=], 159.1 (CH=), 199.0 (WCO), 203.4 (WCO), 299.4 (W=C); IR ($CH_2Cl_2$, cm$^{-1}$): $\tilde{\nu}$ = 2058, 1921; anal. calcd for $C_{20}H_{23}NO_7W$ (573.26): C 41.90, H 4.04, N 2.44; found C 41.63, H 3.86, N 2.30; HREIMS calcd for $C_{20}H_{23}NO_7W$ 573.096337, found 573.099416.

**1,3-Dimorpholino-7-methoxy-2,5,5-trimethylbicyclo[4.1.0]hept-2-ene (18)**: Carbene **11b** (3 equiv, 3 mmol, 870 mg) was added to a 0.1 M solution of diene **1** (1 mmol, 238 mg) in toluene. The solution was refluxed until TLC (silica gel, hexane/ethyl acetate 3:1) showed the absence of **11b** in the reaction mixture (7 h). The work-up was performed as for the cycloheptatrienes **4** to yield 161 mg (48%). $R_f = 0.44$; $^1$H NMR (300 MHz, $CDCl_3$, RT, $CHCl_3$): $\delta = 0.90$ [s, 3H; $(CH_3)_2C$], 0.92 [d, $^3J$(H,H) = 7.7 Hz, 1H; $CH$CH(OMe)], 1.09 [s, 3H; $(CH_3)_2C$], 1.73 (d, $^2J$(H,H) = 15.6 Hz, 1H; $CH_2$), 1.87 (d, $^2J$(H,H) = 15.6 Hz, 1H; $CH_2$), 2.03 (s, 3H; $CH_3C$=), 2.52–2.56 (m, 8H; morpholines), 3.14 (s, 3H; $CH_3O$), 3.35 [d, $^3J$(H,H) = 7.7 Hz, 1H; CHC$H$(OMe)], 3.60 (m, 4H; morpholine), 3.72 (m, 4H; morpholine); $^{13}$C NMR (75 Hz, $CDCl_3$, RT, $CDCl_3$): $\delta = 14.9$ [$(CH_3)_2C$], 26.9 [$(CH_3)_2C$], 29.8 [$(CH_3)_2C$], 30.3 [$(CH_3)C$=], 34.7 ($CH_2$), 36.4 [CH(OMe)], 48.7 (morpholine), 49.9 [C(morpholine)], 50.1 (morpholine), 58.9 [CH(OMe)], 67.2 ($CH_2$, morpholine), 67.7 ($CH_2$, morpholine), 69.7 ($CH_3O$), 120.8 [(Me)C=], 140.8 [(morpholine)C=]; HREIMS calcd for $C_{19}H_{32}N_2O_3$ 336.241273, found 336.241424.

**General Procedure for the Synthesis of Cyclopentenones 20a,b**: Diene **1** (1 mmol) was added to a solution of a Fischer carbene complex **19** (1 mmol) in dry toluene (2 mL) at room temperature. The reaction mixture was stirred at room temperature overnight and concentrated at reduced pressure ($10^{-2}$ Torr). The crude product was dissolved in dry hexane, filtered through a pad of Celite and cooled at −20 °C to induce precipitation of $[Cr(CO)_6]$. The clear solution was decanted and concentrated at reduced pressure (water aspirator), and the crude product obtained was chromatographed in silica gel with hexane/ethyl acetate (3:1).

**4-(1-Cyclohexenyl)-4-methoxy-2-methyl-2-cyclopentenone (20a)**: Pentacarbonyl[1-cyclohexenyl]methoxymethylenechromium(0) (**19a**, 1 mmol, 316 mg) was treated with diene **1** (1 mmol, 238 mg) in toluene for 12 h to yield 111 mg (54%) of **20a**. $R_f = 0.50$; $^1$H NMR (300 MHz, $CDCl_3$, RT, $CHCl_3$): $\delta = 1.52$–$1.70$ (m, 4H; $CH_2CH_2$), 1.83 (s, 3H; $CH_3C$=), 1.95–2.12 (m, 4H; $CH_2C$H=CH$CH_2$), 2.54 (s, 2H; $CH_2CO$), 3.15 (s, 3H; $CH_3O$), 5.64 (m, 1H; $CH_2CH$=), 7.30 [s, 1H; CH=C(Me)]; $^{13}$C NMR (75 MHz, $CDCl_3$, RT, $CDCl_3$): $\delta = 10.0$ ($CH_3C$=), 22.1 ($CH_2$, cyclohexenyl), 22.5 ($CH_2$, cyclohexenyl), 24.2 ($CH_2$, cyclohexenyl), 25.0 ($CH_2$, cyclohexenyl), 46.1 ($CH_2CO$), 51.0 ($CH_3O$), 83.4 [C(OMe)], 124.9 ($CH_2CH$=), 137.6 ($CH_2C$=), 142.9 [(Me)C=], 156.0 [CH=C(Me)], 206.4 (CO); HREIMS calcd for $C_{13}H_{18}O_2$ 206.130671, found 206.130861.

**4-(1-Cyclopentenyl)-4-methoxy-2-methyl-2-cyclopentenone (20b)**: Pentacarbonyl[1-cyclopentenyl]methoxymethylenechromium(0) (**19b**, 1 mmol, 302 mg) was treated with diene **1** (1 mmol, 238 mg) in toluene for 12 h to yield 121 mg (63%). $R_f = 0.46$; $^1$H NMR (300 MHz, $CDCl_3$, RT, $CHCl_3$): $\delta = 1.81$ (s, 3H; $CH_3C$=), 1.90 (quintet, $^3J$(H,H) = 7.3 Hz, 2H; $CH_2CH_2CH_2$), 2.33 (m, 4H; $CH_2CH_2CH_2$), 2.59 (s, 2H; $CH_2CO$), 3.17 (s, 3H; $CH_3O$), 5.63 (m, 1H; $CH_2CH$=), 7.26 [s, 1H; CH=C(Me)]; $^{13}$C NMR (75 MHz, $CDCl_3$, RT, $CDCl_3$): $\delta = 9.9$ ($CH_3C$=), 23.2 ($CH_2$, cyclopentenyl), 31.6 ($CH_2$, cyclopentenyl), 32.4 ($CH_2$, cyclopentenyl), 45.2 ($CH_2CO$), 51.3 ($CH_3O$), 80.8 [C(OMe)], 128.4 ($CH_2CH$=), 142.5 ($CH_2C$=), 144.0 [(Me)C=], 156.1 [CH=C(Me)], 206.1 (CO); HREIMS calcd for $C_{12}H_{16}O_2$ 192.115022, found 192.115361.

**General Procedure for the Reaction of Diene 1 with Carbenes 19c,d**: Carbene **19c** or **19d** (1 equiv) was added to a 0.3 M solution of diene **1** in toluene, the solution was refluxed (for **19c**, method A) or stirred at room temperature (for **19d**, method B) until TLC (silica gel, hexane/ethyl acetate 3:1) showed the absence of the starting complex in the reaction mixture. Then it was worked up as in the case of cycloheptatrienes **4** and cyclopentenones **20a,b**.

**3-Methoxy-2-methyl-3-phenyl-2-cyclopentenone (20c)**: Method A, yield 25% (50 mg). Method B, yield 24% (48 mg). $R_f = 0.53$; $^1$H NMR (200 MHz, $CDCl_3$, RT, $CHCl_3$): $\delta = 1.90$ (d, $^4J$(H,H) = 1.6 Hz, 3H; $CH_3C$=), 2.76 (d, $^2J$(H,H) = 18.4 Hz, 1H; $CH_2$), 2.93 (d, $^2J$(H,H) = 18.4 Hz, 1H; $CH_2$), 3.24 (s, 3H; $CH_3O$), 7.32 (q, $^4J$(H,H) = 1.6 Hz, 1H; CH=), 7.36 (m, 5H; Ph); $^{13}$C NMR (50.3 MHz, $CDCl_3$, RT, $CDCl_3$): $\delta = 10.4$ ($CH_3C$=), 48.1 ($CH_2$), 51.8 ($CH_3O$), 82.9 [C(OMe)], 125.7 (Ph), 127.7 (Ph), 128.6 (Ph), 141.7 (Ph), 143.0 [(Me)C=], 157.1 (CH=), 206.4 (CO); HREIMS calcd for $C_{13}H_{14}O_2$ 202.099373, found 202.098770.

**2-[(1*R**,2*S**)-2-methoxy-1-morpholino-2-phenylcyclopropyl]propanal (*cis*-21)**: Method A, yield 7% (20 mg). Method B, yield 11% (32 mg). $R_f = 0.40$; $^1$H NMR (300 MHz, $CDCl_3$, RT, $CHCl_3$): $\delta = 1.01$ (d, $^2J$(H,H) = 6.4 Hz, 1H; $CH_2$), 1.36 (d, $^3J$(H,H) = 7.3 Hz, 3H; $CH_3CH$), 1.52 (d, $^2J$(H,H) = 6.4 Hz, 1H; $CH_2$), 2.32–2.44 (m, 2H; morpholine), 2.52–2.62 (m, 2H; morpholine), 2.81 (q, $^3J$(H,H) = 7.3 Hz, 1H; $CH_3CH$), 2.90–3.00 (m, 2H; morpholine), 3.10–3.16 (m, 2H; morpholine), 3.17 (s, 3H; $CH_3O$), 7.21–7.45 (m, 5H; Ph), 10.00 (s, 1H; CHO); $^{13}$C NMR (75 MHz, $CDCl_3$, RT, $CDCl_3$): $\delta = 11.8$ ($CH_3CH$), 22.9 ($CH_2$, cyclopropane), 49.5 ($CH_2$, morpholine), 50.6 (CHMe), 54.7 ($CH_3O$), 56.3 [C(morpholine)], 67.0 ($CH_2$, morpholine), 74.1 [C(OMe)], 126.9 (Ph), 127.2 (Ph), 127.9 (Ph), 136.5 (Ph), 205.2 (CHO); HREIMS calcd for $C_{17}H_{23}NO_3$ 289.167781, found 289.167862.

**2-[(1*R**,2*R**)-2-methoxy-1-morpholino-2-phenylcyclopropyl]propanal (*trans*-21)**: Method A, yield 6% (17 mg). Method B, yield 9% (26 mg). $R_f = 0.34$ ($SiO_2$, hexane/EtOAc 3:1); $^1$H NMR (200 MHz, $CDCl_3$, RT, $CHCl_3$): $\delta = 1.13$ (d, $^2J$(H,H) = 6.4 Hz, 1H; $CH_2$), 1.18 (d, $^3J$(H,H) = 7.0 Hz, 3H; $CH_3CH$), 1.41 (d, $^2J$(H,H) = 6.4 Hz, 1H; $CH_2$), 2.16–2.32 (m, 2H; morpholine), 2.45–2.58 (m, 2H; morpholine), 2.90 (q, $^3J$(H,H) = 7.0 Hz, 1H; $CH_3CH$), 3.10–3.22 (m, 2H; morpholine), 3.13 (s, 3H; $CH_3O$), 3.30–3.40 (m, 2H; morpholine), 7.28–7.43 (m, 5H; Ph), 9.85 (s, 1H; CHO); $^{13}$C NMR (50.3 MHz, $CDCl_3$, RT, $CDCl_3$): $\delta = 14.0$ ($CH_3CH$), 20.5 ($CH_2$, cyclopropane), 43.1 (CHMe), 48.5 (morpholine), 54.4 ($CH_3O$), 57.4 [C(morpholine)], 66.8 (morpholine), 72.0 [C(OMe)], 126.8 (Ph), 127.2 (Ph), 128.5 (Ph), 136.2 (Ph), 203.6 (CHO); HREIMS calcd for $C_{17}H_{23}NO_3$ 289.167781, found 289.166998.

**General Procedure for the Reaction of Diene 1 with Carbenes 22: Method A**: Carbene **22** (1 equiv) was added to a 0.3 M solution of diene **1** in toluene; the deep violet solution was refluxed for 2 h. Then it was worked up as for cycloheptatrienes **4** to obtain **23**, **24** and **25**.

**Reaction of carbene complex 22a with diene 1 (method A)**: Pentacarbonyl[1-methoxyethylidene]chromium(0) (1 mmol, 250 mg) **22a** was treated with **1** (1 mmol, 238 mg) to obtain **23a** (50 mg, 24%) and **24a** (48 mg, 23%).

**1,5-Dimethyl-2-methoxy-1-morpholino-2,4-cyclopentadiene (23a)**: $R_f = 0.48$; $^1$H NMR (300 MHz, $CDCl_3$, RT, $CHCl_3$): $\delta = 1.20$ [s, 3H; $CH_3C$(morpholine)], 1.75 (d, $^4J$(H,H) = 2.6 Hz, 3H; $CH_3C$=), 2.60 (m, 4H; morpho-

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line), 3.64 (s, 3H; $CH_3O$), 3.66 (m, 4H; morpholine), 4.95 [d, $^3J(H,H)$ = 2.2 Hz, 1H; CH=C(OMe)], 5.72 [dd, $^3J(H,H)$ = 2.2 Hz, $^4J(H,H)$ = 2.6 Hz, 1H, CH=C(Me)]; $^{13}C$ NMR (50.3 MHz, $CDCl_3$, RT, $CDCl_3$): $\delta$ = 12.6 [$CH_3C$(morpholine)], 19.0 ($CH_3C$=), 46.6 ($CH_2$, morpholine), 56.3 ($CH_3O$), 67.9 ($CH_2$, morpholine), 70.5 [(Me)$C$(morpholine)], 95.0 [CH=C(OMe)], 122.9 [CH=C(Me)], 138.3 [(Me)C=], 170.0 [(MeO)C=]; HREIMS calcd for $C_{12}H_{19}NO_2$ 209.141569, found 209.141822.

**5-Methoxy-2-methyl-1-morpholinobicyclo[3.1.0]hex-2-ene (24a)**: $R_f$ = 0.31; $^1H$ NMR (200 MHz, $CDCl_3$, RT, $CHCl_3$): $\delta$ = 0.39 (d, $^2J(H,H)$ = 4.6 Hz, 1H; $CH_2$, cyclopropane), 1.23 (d, $^2J(H,H)$ = 4.6 Hz, 1H; $CH_2$, cyclopropane), 1.86 (s, 3H; $CH_3C$=), 2.45 (d, $^2J(H,H)$ = 17.2 Hz, 1H; $CH_2$, cyclopentene), 2.61 (d, $^2J(H,H)$ = 17.2 Hz, 1H; $CH_2$, cyclopentene), 2.90 (m, 4H; morpholine), 3.43 (s, 3H; $CH_3O$), 3.68 (m, 4H; morpholine), 5.04 (s, 1H; CH=); $^{13}C$ NMR (75 MHz, $CDCl_3$, RT, $CDCl_3$): $\delta$ = 16.7 ($CH_3C$=), 25.5 ($CH_2$, cyclopropane), 37.5 ($CH_2$, cyclopentene) 50.1 ($CH_2$, morpholine), 56.6 ($CH_3O$), 59.9 [C(OMe)], 67.5 ($CH_2$, morpholine), 71.0 [C(morpholine)], 120.8 (CH=), 144.3 [(Me)C=]; HREIMS calcd for $C_{12}H_{19}NO_2$ 209.141569, found 209.141824.

**Reaction of carbene complex 22b with diene 1 (method A)**: Pentacarbonyl[1-benzyloxyethylidene]chromium(0) (**22b**, 1 mmol, 326 mg) was treated with **1** (1 mmol, 238 mg) to obtain **23b** (65 mg, 23%), **24b** (43 mg, 15%) and **25** (18 mg, 10%).

**2-Benzyloxy-1,5-dimethyl-1-morpholino-2,4-cyclopentadiene (23b)**: $R_f$ = 0.50; $^1H$ NMR (200 MHz, $CDCl_3$, RT, $CHCl_3$): $\delta$ = 1.27 [s, 3H; $CH_3C$(morpholine)], 1.74 (s, 3H; $CH_3C$=), 2.68 (m, 4H; morpholine), 3.68 (m, 4H; morpholine), 4.80 (d, $^2J(H,H)$ = 12.0 Hz, 1H; $CH_2Ph$), 4.93 (d, $^2J(H,H)$ = 12.0 Hz, 1H; $CH_2Ph$), 5.02 [d, $^3J(H,H)$ = 2.2 Hz, 1H; CH=C(OMe)], 5.76 [m, 1H; CH=C(Me)], 7.43 (m, 5H; Ph); $^{13}C$ NMR (50.3 MHz, $CDCl_3$, RT, $CDCl_3$): $\delta$ = 12.3 [$CH_3C$(morpholine)] 19.1 ($CH_3C$=), 46.7 ($CH_2$, morpholine), 67.8 ($CH_2$, morpholine), 70.6 [(Me)C(morpholine)], 70.9 ($CH_2Ph$), 96.2 [CH=C(OMe)], 122.7 [CH=C(Me)], 127.1 (Ph), 127.6 (Ph), 128.3 (Ph), 136.9 (Ph), 138.5 [(Me)C=], 168.6 [(MeO)C=]; HREIMS calcd for $C_{18}H_{23}NO_2$ 285.172867, found 285.172939.

**5-Benzyloxy-2-methyl-1-morpholinobicyclo[3.1.0]hex-2-ene (24b)**: $R_f$ = 0.44; $^1H$ NMR (300 MHz, $CDCl_3$, RT, $CHCl_3$): $\delta$ = 0.44 (d, $^2J(H,H)$ = 4.7 Hz, 1H; $CH_2$, cyclopropane), 1.37 (d, $^2J(H,H)$ = 4.7 Hz, 1H; $CH_2$, cyclopropane), 3.70 (q, $^4J(H,H)$ = 2.2 Hz, $^5J(H,H)$ = 2.2 Hz, 3H; $CH_3C$=), 2.45 (dquintet, $^2J(H,H)$ = 17.2 Hz, $^3J(H,H)$ = 2.2 Hz, $^5J(H,H)$ = 2.2 Hz, 1H; $CH_2$, cyclopentene), 2.63 (dquintet, $^2J(H,H)$ = 17.2 Hz, $^3J(H,H)$ = 2.2 Hz, $^5J(H,H)$ = 2.2 Hz, 1H; $CH_2$, cyclopentene), 2.80–3.45 (m, 4H; morpholine), 3.60–3.75 (m, 4H; morpholine), 4.68 (s, 2H; $CH_2Ph$), 5.02 (sextet, $^3J(H,H)$ = 2.2 Hz, $^4J(H,H)$ = 2.2 Hz, 1H; CH=), 7.20–7.39 (m, 5H; Ph); $^{13}C$ NMR (75 MHz, $CDCl_3$, RT, $CDCl_3$): $\delta$ = 16.2 ($CH_3C$=), 25.9 ($CH_2$, cyclopropane), 38.6 ($CH_2$, cyclopentene), 50.1 ($CH_2$, morpholine), 60.3 [C(morpholine)], 67.8 ($CH_2$, morpholine), 70.5 [C(OBn)], 71.4 ($CH_2Ph$), 120.5 (CH=), 127.1 (Ph), 127.2 (Ph), 128.1 (Ph), 139.0 (Ph), 144.3 [(Me)C=]; HREIMS calcd for $C_{18}H_{23}NO_2$ 285.172867, found 285.172219.

***N*-(2-methylphenyl)morpholine (25)**: $R_f$ = 0.65, UV developed; $^1H$ NMR (300 MHz, $CDCl_3$, RT, $CHCl_3$): $\delta$ = ($CDCl_3$) 2.36 (s, 3H; $CH_3$), 2.94 (t, $^3J(H,H)$ = 4.5 Hz, 4H; morpholine), 3.89 (t, $^3J(H,H)$ = 4.5 Hz, 4H; morpholine), 6.95–7.10 (m, 2H; Ar), 7.15–7.30 (m, 2H; Ar); $^{13}C$ NMR (50.3 MHz, $CDCl_3$, RT, $CDCl_3$): $\delta$ = 17.8 ($CH_3$), 52.1 ($CH_2$, morpholine), 67.4 ($CH_2$, morpholine), 118.8 (CH), 123.3 (CH), 126.5 (CH), 131.0 (CH), 132.5 (C), 151.1 (C); HREIMS calcd for $C_{11}H_{15}NO$ 177.115356, found 177.115341.

**Reaction of carbene complex 22c with diene 1 (method A)**: Pentacarbonyl[1-*tert*-butoxyethylidene]chromium(0) **22c** (1 mmol, 292 mg) was treated with 2-methyl-1,3-dimorpholino-1,3-butadiene **1** (1 mmol, 238 mg) to obtain **23c** (78 mg, 31%).

**2-*tert*-Butoxy-1,5-dimethyl-1-morpholino-2,4-cyclopentadiene (23c)**: $R_f$ = 0.66; ($SiO_2$, hexane/EtOAc 3:1); $^1H$ NMR (300 MHz, $CDCl_3$, RT, $CHCl_3$): $\delta$ = 1.13 [s, 3H; $CH_3C$(morpholine)], 1.40 [s, 9H; $C(CH_3)_3$], 1.67 (s, 3H; $CH_3C$=), 2.62 (m, 4H; morpholine), 3.62 (m, 4H; morpholine), 4.90 [s, 1H; CH=C(OMe)], 5.70 [s, 1H; CH=C(Me)]; $^{13}C$ NMR (50.3 MHz, $CDCl_3$, RT, $CDCl_3$): $\delta$ = 12.1 [$CH_3C$(morpholine)], 19.3 ($CH_3C$=), 27.8 [$C(CH_3)_3$] 46.5 ($CH_2$, morpholine), 68.1 ($CH_2$, morpholine), 71.3 [$CH_3C$(morpholine)], 78.0 [$C(CH_3)_3$], 97.2 [CH=C(OMe)], 123.2 [CH=C(Me)], 137.1 [(Me)C=], 164.4 [(MeO)C=]; $C_{15}H_{25}NO_2$ (251): calcd C 71.67, H 10.02, N 5.57; found C 72.01, H 9.78, N 5.42.

**Reaction of carbene complex 22d with diene 1 (method A)**: Pentacarbonyl[1-*tert*-butoxyethylidene]tungsten(0) (1 mmol, 382 mg) **22d** was treated with 2-methyl-1,3-dimorpholino-1,3-butadiene **1** (1 mmol, 238 mg) to obtain **23a** (46 mg, 22%), **24a** (42 mg, 20%) and **25** (30 mg, 17%).

**General procedure for reaction of diene 1 with carbene complexes 22 (Method B)**: To a solution of carbene **22** in $CH_2Cl_2$ (1 mL) and hexane (5 mL), diene **1** (1 mmol) was added; the colour turned to violet. It was stirred for 1 h at room temperature and then cooled at −20 °C overnight; compounds **26** were obtained as dark violet solids.

**Pentacarbonyl[2,4-dimethyl-1-methoxy-5-morpholino-2,4-pentadienylidene]-chromium(0) (26a)**: Pentacarbonyl[1-methoxyethylidene]chromium(0) (**22a**, 1 mmol, 250 mg) was treated with **1** (1 mmol, 0.238 g) to yield 0.369 g (92%). $^1H$ NMR (300 MHz, $CDCl_3$, RT, $CHCl_3$): $\delta$ = 1.87 (s, 3H; $CH_3C$=), 2.93 (s, 3H; $CH_3C$=), 3.49 (t, $^3J(H,H)$ = 3.9 Hz, 4H; morpholine), 3.80 (t, $^3J(H,H)$ = 3.9 Hz, 4H; morpholine), 4.24 (s, 3H; $CH_3O$), 6.74 (d, $^3J(H,H)$ = 13.3 Hz, 1H; CH=), 8.00 (d, $^3J(H,H)$ = 13.3 Hz, 1H; CH=); $^{13}C$ NMR (75 MHz, $CDCl_3$, RT, $CDCl_3$): $\delta$ = 16.2 ($CH_3C$=), 18.2 ($CH_3C$=), 52.0 ($CH_2$, morpholine), 61.3 ($CH_3O$), 66.9 ($CH_2$, morpholine), 112.0 [(Me)C=], 126.5 (CH=), 152.8 (CH=), 167.0 [(Me)(morpholine)C=], 218.9 (CrCO), 224.8 (CrCO), 303.0 (Cr=C); IR ($CH_2Cl_2$, $cm^{-1}$): $\tilde{\nu}$ = 2048, 1923; $C_{17}H_{19}NO_7Cr$ (401): C 50.88, H 4.77, N 3.49; found C 51.02, H 4.50, N 3.47.

**Pentacarbonyl[2,4-dimethyl-1-benzyloxy-5-morpholino-2,4-pentadienlyden]-chromium(0) (26b).** Pentacarbonyl[1-benzyloxyethylidene]chromium(0) **22b** (1 mmol, 326 mg) was treated with **1** (1 mmol, 238 mg) to yield 467 mg (98%). $^1H$ NMR (200 MHz, $CDCl_3$, RT, $CHCl_3$): $\delta$ = 1.86 (s, 3H; $CH_3C$=), 2.28 (s, 3H; $CH_3C$=), 3.48 (t, $^3J(H,H)$ = 4.7 Hz, 4H; morpholine), 3.75 (t, $^3J(H,H)$ = 4.7 Hz, 4H; morpholine), 5.50 (s, 2H; $CH_2Ph$), 6.79 (d, $^3J(H,H)$ = 13.5 Hz, 1H; CH=), 7.35–7.55 (m, 5H; Ph), 8.04 (d, $^3J(H,H)$ = 13.5 Hz, 1H; CH=); $^{13}C$ NMR (50.3 MHz, $CDCl_3$, RT, $CDCl_3$): $\delta$ = 16.3 ($CH_3C$=), 18.4 ($CH_3C$=), 52.2 ($CH_2$, morpholine), 66.9 ($CH_2$, morpholine), 75.7 ($CH_2Ph$), 112.1 [(Me)C=], 126.5 (CH=), 127.5 (Ph), 128.0 (Ph), 128.5 (Ph), 136.4 (Ph), 153.9 (CH=), 167.6 [(Me)(morpholine)C=], 219.0 (CrCO), 224.8 (CrCO), 300.4 (Cr=C); IR ($CH_2Cl_2$, $cm^{-1}$): $\tilde{\nu}$ = 2054, 1921; anal. calcd for $C_{23}H_{23}NO_7Cr$ (477): C 57.86, H 4.86, N 2.93; found C 57.59, H 4.60, N 2.81; HREIMS calcd for $C_{23}H_{23}NO_7Cr$ 477.087962, found 477.088123.

**Pentacarbonyl[1-*tert*-butoxy-4,5-dimethyl-5-morpholino-2,4-pentadienylidene]-chromium(0) (26c)**: Pentacarbonyl[1-*tert*-butoxyethylidene]chromium(0) (**22c**, 1 mmol, 292 mg) was treated with **1** (1 mmol, 238 mg) to yield 530 mg (73%). $^1H$ NMR (200 MHz, $CDCl_3$, RT, $CHCl_3$): $\delta$ = 1.62 [s, 9H; $(CH_3)_3C$], 1.87 (s, 3H; $CH_3C$=), 2.34 (s, 3H; $CH_3C$=), 3.49 (m, 4H; morpholine), 3.82 (m, 4H; morpholine), 6.76 (d, $^3J(H,H)$ = 13.3 Hz, 1H; CH=), 8.33 (d, $^3J(H,H)$ = 13.3 Hz, 1H; CH=); $^{13}C$ NMR (50.3 MHz, $CDCl_3$, RT, $CDCl_3$): $\delta$ = 16.5 ($CH_3C$=), 18.0 ($CH_3C$=), 29.9 [$(CH_3)_3C$], 51.9 ($CH_2$, morpholine), 67.0 ($CH_2$, morpholine), 87.0 [$(CH_3)_3C$], 112.4 [(Me)C=], 126.2 (CH=), 164.4 (CH=), 165.3 [(Me)(morpholine)C=], 219.8 (CrCO), 225.4 (CrCO), 305.12 (Cr=C); IR ($CH_2Cl_2$, $cm^{-1}$): $\tilde{\nu}$ = 2046, 1927; $C_{20}H_{25}NO_7Cr$ (443): C 54.17, H 5.68, N 3.16; found C 54.12, H 5.47, N 2.94.

**Pentacarbonyl[1-methoxy-2,4-dimethyl-5-morpholino-2,4-pentadienylidene]-tungsten(0) (26d)**: Pentacarbonyl[1-methoxyethylidene]tungsten(0) (**22d**, 1 mmol, 382 mg) was treated with **1** (1 mmol, 238 mg) to yield 506 mg (95%). $^1H$ NMR (300 MHz, $CDCl_3$, RT, $CHCl_3$): $\delta$ = 1.88 (s, 3H; $CH_3C$=), 2.23 (s, 3H; $CH_3C$=), 3.50 (t, $^3J(H,H)$ = 4.7 Hz, 4H; morpholine), 3.79 (t, $^3J(H,H)$ = 4.7 Hz, 4H; morpholine), 4.22 (s, 3H; $CH_3O$), 6.70 (d, $^3J(H,H)$ = 13.5 Hz, 1H; CH=), 8.01 (d, $^3J(H,H)$ = 13.5 Hz, 1H; CH=); $^{13}C$ NMR (75 MHz, $CDCl_3$, RT, $CDCl_3$): $\delta$ = 16.3 ($CH_3C$=), 18.4 ($CH_3C$=), 52.1 ($CH_2$, morpholine), 63.6 ($CH_3O$), 66.9 ($CH_2$, morpholine), 112.0 [(Me)C=], 129.7 (CH=), 153.5 (CH=), 167.4 [(Me)(morpholine)C=], 199.4 (WCO), 204.5 (WCO), 280.5 (W=C); IR ($CH_2Cl_2$, $cm^{-1}$): $\tilde{\nu}$ = 2056, 1927; $C_{17}H_{19}NO_7W$ (533): calcd C 38.27, H 3.59, N 2.63; found C 38.33, H 3.47, N 2.76.

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