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The Chromium and Tungsten Pentacarbonyl Groups as Reactivity Auxiliaries in [2 + 2] Cycloadditions[†]

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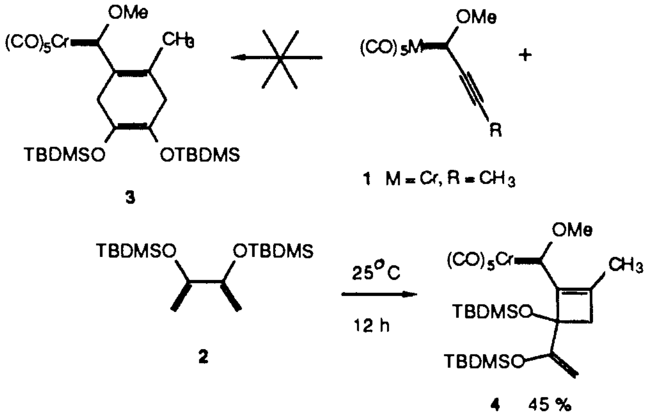
The Diels–Alder reactions of chromium and tungsten carbene complexes with 1,3-dienes occur with high regio- and stereoselectivities and are useful as synthons for acrylate and alkynoate esters as well as for the preparation of elaborated carbene complexes to be used in subsequent annulations.[1] In an effort to apply this reaction to the synthesis of ecdysteroids, we were led to examine the reaction of the propynyl chromium complex **1**[2] with



3

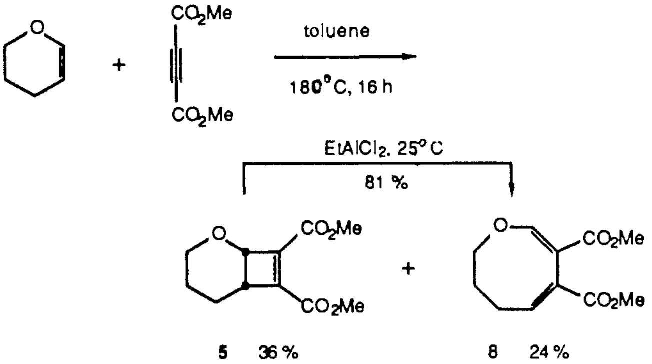
1 M = Cr, R = CH_3

2

4 45 %

2,3-bis(*tert*-butyldimethylsilyl)oxy)-1,3-butadiene (**2**). It was most unexpected to find that this reaction led to the formation of the [2 + 2] rather than the [4 + 2] cycloadduct because dienes of the type **2** are not known to normally give [2 + 2] cycloadducts[3] with dienophiles and because [2 + 2] cycloadditions of either alkenyl or alkynyl carbene complexes are unknown. This result was also unanticipated since the transformation that would be expected to be competitive with [4 + 2] cycloadditions is cyclopropanation.[1i]

Although the range of useful alkenes can be greatly expanded when the [2 + 2] cycloaddition of alkenes and alkynes are catalyzed by main group[5] and transition-metal[6] Lewis acids, the thermal [2 + 2] cycloaddition of alkenes and alkynes is not a particularly useful reaction and is limited mainly to the reactions of enamines, ynamines, and halogenated alkenes.[7] There are two reports of cycloadditions of ketene acetals with acetylenic esters,[8] and only three reports with an enol ether.[9] For example, the thermal [2 + 2] cycloaddition of dihydropyran and DMADC was reported to give both the cyclobutene (**5**) and its ring-opened isomer at 180 °C.[9b] The great ease with which the enol ether function of diene **2** reacts with the complex **1** suggested that the thermal [2 + 2] cycloadditions of alkynyl carbene complexes and olefins may be a reaction of broader scope and utility than the reactions of their ester analogues.



5 36 %

8 24 %

Alkynyl carbene complexes will give moderate to high yields of [2 + 2] cycloaddition products with a range of enol ethers under very mild conditions as indicated by the data in Table I. In addition to dihydropyran, large rate enhancements can be seen for alkynyl carbene complexes compared to alkynyl esters with ketene diethyl acetal. The reaction with ethyl propiolate was reported to require heating at 50 °C for 29 h, whereas the corresponding reaction with **7** was extremely fast and was, in effect, carried out as a titration. Olefins such as cycloheptene or vinyl acetate did not react with **7** at room temperature; however, these reactions have not been explored under more forcing conditions. Cyclopropanation and olefin metathesis would be processes[4] that would be expected to be competitive;[1i] however, we have not observed any cyclopropanation products from the reactions in Table I.

With the exception of ethyl vinyl ether, all of the olefins examined afforded the expected [2 + 2] cycloadducts. Adducts from the reaction with ethyl vinyl ether was unstable with respect to ring-opening at room temperature and provided dienyl complexes directly. The electrocyclic ring-opening of the cyclobutenyl carbene complex **11** could be induced by warming to 50 °C. However, at this temperature, the chelation complex **10** was the major product. The stereochemistry about the dienyl carbene substituents is assigned as *Z* since these complexes readily lose carbon monoxide and form chelates.[1c,10] This stereochemical assignment is also consistent with the known propensity of alkoxy substituents to rotate out in electrocyclic ring-openings of cyclobutenes.[11] The dienyl complexes **21**, **22**, and **24** are much more reluctant to form chelates than the complexes **10** and **13** which is presumably a result of the steric differences of ethyl versus methyl as oxygen substituents.

Alkynyl carbene complexes can serve as synthons for alkynyl esters in [2 + 2] cycloadditions. For example, complex **19** can

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[†] Dedicated to Professor E. O. Fischer on the occasion of his 70th birthday.

[‡] National Institutes of Health Predoctoral Fellow, 1984–1988.

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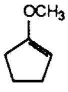
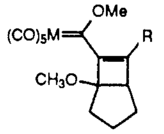
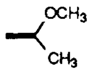
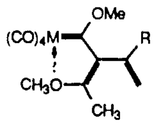
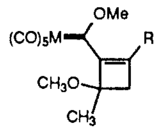
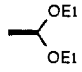
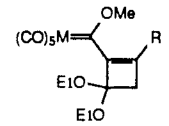
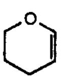
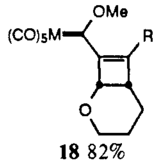
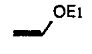
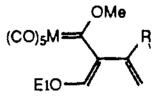
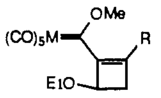
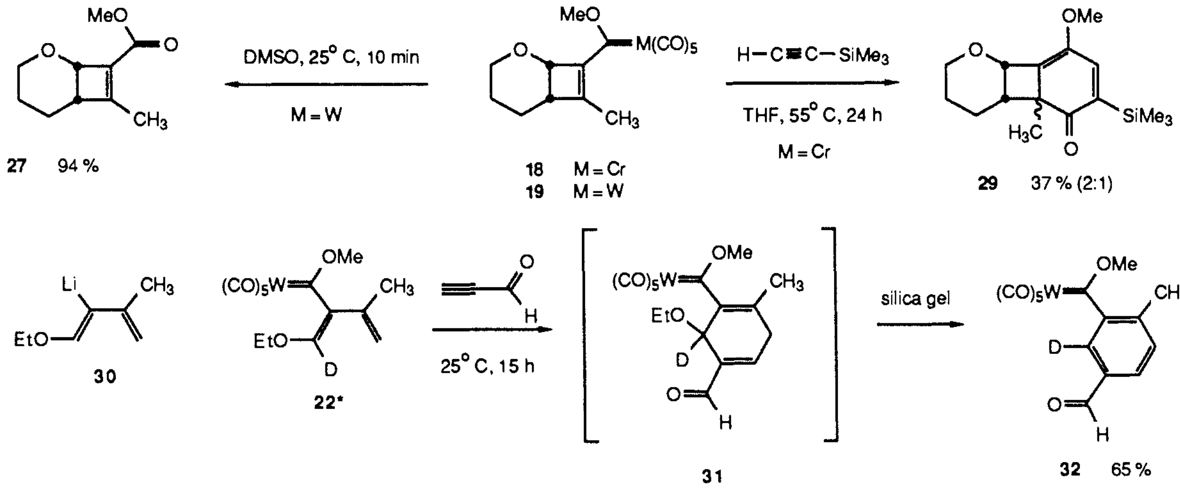
Table I. [2 + 2] Cycloadditions of Chromium and Tungsten Alkynyl Complexes[a]

entry	alkyne complex	olefin	time	2-dienyl complex, yield[b]	2-cyclobutenyl complex, yield[b]
1	**7**, M = W; R = CH$_3$		3 h		 **8** 87%
2	**1**, M = Cr; R = CH$_3$		6 h		 **9** 63%
3	**7**, M = W; R = CH$_3$		2 h	**10**[c] <2%	**11** 80%
4	**12**, M = W; R = Ph		2 days	**13**[d] 34%	**14**[e] 14%
5	**15**; M = W; R = *t*-Bu		2 days		**16** 53%
6	**1**, M = Cr; R = CH$_3$		~10 min[f]		 **17** 73%
7	**1**, M = Cr; R = CH$_3$		24 h		 **18** 82%
8	**7**, M = W; R = CH$_3$		6 h		**19** 97%
9	**1**, M = Cr; R = CH$_3$		29 h	 **21** 32%	
10	**7**, M = W; R = CH$_3$		4 h	**22** 40%	**23** 6%
11	**20**, M = W; R = SiMe$_3$		14 h	**24** 56%	

[a] Unless otherwise specified all reactions were carried out at room temperature under argon with the carbene complex dissolved in excess olefin (10 equiv). [b] All yields refer to products that are purified by flash chromatography on silica gel. [c] Not detected in the crude reaction mixture by (<2%). [d] Obtained as a 3:1 mixture of chelated to nonchelated complexes which was characterized by allowing the mixture to go completely to the chelated complex **13**. [e] Characterized only by ^{1}H NMR as this complex was unstable with respect to ring-opening. [f] A 0.2 M solution of the carbene complex in methylene chloride was titrated with the ketene acetal at room temperature until all starting material was gone; complex **17** was sensitive to silica gel but could be purified (73%) by chromatography on silica gel at −60 °C.

Scheme I



be oxidatively cleaved in DMSO^{1a,12} at 25 °C within 10 min of dissolution to give the ester **27** in 94% yield. The overall efficacy of complex **1** as a synthon for methyl tetrolate is demonstrated by the fact that the ester **27** can be obtained in 90% overall yield from dihydropyran in two steps that can both be performed at room temperature.

Preliminary investigations reveal that the [2 + 2] cycloadducts could have the potential for unique synthetic applications over and above their service as synthons for alkynyl esters. The chromium cyclobutenyl carbene complex **18** can be annulated with trimethylsilylacetylene to give the rather interesting tricyclic

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dienone **29** as a 2:1 mixture of diastereomers.[13] Moreover, the [2 + 2] cycloaddition/electrocyclic ring-opening provides a straightforward method for the preparation of a variety of the previously unknown 2-butadienyl complexes. Specifically, 2-butadienyl carbene complexes of the type **22** would be difficult to prepare by the standard Fischer method since organolithiums of the type **30** would be expected to be unstable with respect to β-elimination at temperatures necessary for addition to group 6 carbonyls. We have found that these complexes will undergo Diels–Alder reactions with highly activated dienophiles (benzoquinone, dimethyl acetylene dicarboxylate, acrolein, maleic anhydride). As revealed by the reaction of complex **22*** with propargyl aldehyde, the regioisomer obtained in these reactions is not the one expected under the influence of an electron-withdrawing group in the 2-position of the diene.[14] Apparently, in diene **22*** the combined effect of the ethoxy and methyl groups dominates over that of the tungsten–carbene functionality in controlling the regiochemistry. This may be for electronic reasons, or perhaps more likely may be due to the combined effect of these groups on the conformation about the diene–carbene carbon bond. Further investigations of the [2 + 2] cycloadditions of chromium and tungsten carbene complexes and the synthetic utility of the organometallic complexes derived therefrom are currently ongoing.

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Supplementary Material Available: Spectral data for all new compounds (8 pages). Ordering information is given on any current masthead page.

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Generation, Alkyne Cycloaddition, Arene C–H Activation, N–H Activation, and Dative Ligand Trapping Reactions of the First Monomeric Imidozirconocene ($Cp_2Zr{=}NR$) Complexes

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Many metal-oxo (M=O) and -imido (M=NR) complexes are known, but in most the M=X linkages are notoriously inert. The absence from the literature of monomeric group IV metallocenes of this class ($(\eta^5\text{-}C_5R_5)_2M{=}O$ and $(\eta^5\text{-}C_5R_5)_2M{=}NR'$, M = Ti, Zr, Hf) suggests that if these species could be generated, they might exhibit more extensive chemistry than do oxo and imido complexes that are presently known. We now wish to report the successful generation of imidozirconocene complexes, a study of their chemical reactivity, and the isolation and X-ray structure determination of the monomeric THF-trapped adduct $Cp_2(THF)Zr{=}N(t\text{-Bu})$ ($Cp = \eta^5\text{-}C_5H_5$).

The chemistry we have observed is summarized in Scheme I. Our starting material, the zirconocene methyl amide complex **1a**, can be generated by heating Cp_2ZrMe_2[1] with 1 equiv of 4-*tert*-butylaniline in benzene at 85 °C. This results in loss of 1 equiv of methane and generation of the zirconocene methyl amide in situ, as observed by ^1H NMR spectrometry. Alternatively, the methyl amides **1a–c** can be prepared in gram quantities by treatment of $Cp_2Zr(CH_3)(Cl)$[2] with the lithium salt of the appropriate amine in THF at 25 °C (24 h for **1a** and **1c**; 2.5 h for **1b**). In the case of **1a**, heating the methyl amide at 85 °C for 3 days in benzene leads to elimination of a second equivalent of methane[3] and formation of a kelly-green compound that crystallizes from the solution in 70%[4] yield upon cooling to room temperature. Single crystals suitable for an X-ray diffraction study of **2a** were grown by slow cooling of a toluene solution of the complex from 85 °C to room temperature. The structure shows that **2a** is the bridging imido dimer indicated in Scheme I; an ORTEP drawing is included.[5] Some atoms in the molecule could not be located precisely due to excessive thermal motion (see Supplementary Material for details). However, the Zr–N–Zr portion of the structure is well-behaved, and, as predicted, the imido bridges are symmetric.[6] The Zr–N distances of 2.098 (2) and 2.093 (2) Å as well as the N–Zr–N angle of 80.56 (7)° are typical of bridging imido dimers.[7]

It seems likely that **2a** is formed by generation and dimerization of $Cp_2Zr{=}N\text{-}Ar$. This hypothesis was reinforced by the chemistry of the sterically more hindered *tert*-butylamido complex **1b**. In benzene at 85 °C, thermolysis of **1b** does not lead to **2b**, the dimer corresponding to **2a**, but instead gives methane and the phenyl(amido)zirconocene complex $Cp_2Zr(NHCMe_3)(Ph)$, **3**, isolated in 61% yield[8] after recrystallization from toluene layered with hexane at −30 °C. In this reaction, the reactive Zr=N linkage apparently induces cleavage of the C–H bond in benzene, leading to the phenyl-substituted product.[9] Alkynes also serve to trap the imido complex efficiently. In the presence of a number of internal alkynes, heating methyl amides **1a–c** leads to azametallacyclobutene complexes **4a–c**, **5b**,**c**, and **6b** in good yield.[10] The unsaturated heterometallacycles are intensely colored, possibly due to charge transfer from the azaallyl moiety to the empty orbital on the formally 16-electron zirconium center.[11] In the

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(1) Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1971**, *34*, 155.

(2) $Cp_2Zr(Me)(Cl)$ was prepared by the reaction of Cp_2ZrMe_2 with Cp_2ZrCl_2. A 0.5 M solution in each reagent in toluene was heated to 130 °C for 35 h. $Cp_2Zr(Me)(Cl)$ can be isolated in >90% yield by recrystallization from toluene/hexanes. Jordan, R. F. *J. Organomet. Chem.* **1985**, *294*, 321.

(3) (a) For a similar reaction, see: (a) Mayer, J. M.; Curtis, L. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2651. For α-elimination to generate the isolobal alkylidene complexes, see: (b) Bulls, A. R.; Schaefer, W. P.; Serfas, M.; Bercaw, J. E. *Organometallics* **1987**, *6*, 1219. (c) Gibson, C. P.; Dabbagh, G.; Bertz, S. H. *J. Chem. Soc., Chem. Commun.* **1988**, 603. (d) Bertz, S. H.; Dabbagh, G.; Gibson, C. P. *Organometallics* **1988**, *7*, 563. With analogous complexes having groups with β-hydrogens, β-elimination often occurs at lower temperature; see: (e) Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1988**, *110*, 3171 and references therein. (f) Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; Van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21.

(4) Full characterization by spectrometry and elemental analysis has been carried out on all new complexes reported; data are provided as Supplementary Material. All yields are for recrystallized complexes except where noted.

(5) The X-ray diffraction study was carried out at the University of California, Berkeley, X-ray diffraction facility (CHEXRAY). Crystal data for bridging imido dimer **2a**: $P2_1/n$, $V = 2042.9$ (9) Å, Mo Kα ($\lambda = 0.71073$ Å) $\mu = 5.3\ \text{cm}^{-1}$, $d_{\text{calcd}} = 1.36\ \text{g cm}^{-1}$, $a = 13.4185$ (16) Å, $b = 9.3796$ (13) Å, $c = 16.9932$ (23) Å, $\beta = 107.224$ (10)°, $T = 25$ °C, $Z = 2$; the final residuals for 233 variables refined against the 2375 data for which $F^2 > 3\sigma(F^2)$ were $R = 0.0428$, wR = 0.0689, and GOF = 3.74. The R value for all 2664 data was 5.30%. Details of the structure determination are provided as Supplementary Material.

(6) Thorn, D. L.; Nugent, W. A.; Harlow, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 357.

(7) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123.

(8) In the reactions involving the alkyl amides all yields are reported as recrystallized yield of the product based on $Cp_2ZrMeCl$; the intermediate alkyl amides were not isolated.

(9) Preliminary attempts to activate methane have been unsuccessful. Heating **9** to 95 °C under 18 atm of methane in cyclohexane leads to intractable products. Further efforts toward activation of sp^3 C–H bonds is presently under investigation.

(10) Analogous cycloaddition chemistry has been observed for the isoelectronic titanium methylidene complex $Cp_2Ti{=}CH_2$; this species does not appear to react with C–H bonds. (a) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. (b) Howard, T. R.; Lee, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 6876. (c) Finch, W. C.; Anslyn, E. V.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 2406 and references therein.