NMR spectrum at +146 ppm, with ^{29}Si and ^{77}Se satellites, and triplets in the ^{29}Si and ^{77}Se NMR spectra. The observed $^1J_{^{31}P-^{77}Se}$ value of 83 Hz seems to be one of the lowest ever recorded. Normal P-Se bonds in acyclic molecules show ^1J values of -200 to -400 Hz,[13] but smaller values, -100 to -270 Hz, have been observed for phosphorus-selenium rings and cages.[14]

The examples of **2a**, **3**, and **4** indicate that reactions of **1** that break the P-P bond and lead to asterane-like molecules may be fairly general. Additional examples of such structures can be expected in the future.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Contract No. AFOSR-89-0004 and National Science Foundation Grant No. CHE-8922737.

Supplementary Material Available: Structure determination summary, Table I containing atomic coordinates, equivalent isotropic displacement factors, and occupanices, Table II containing bond lengths, Table III containing bond angles, and a thermal ellipsoid drawing for **2** (11 pages). Ordering information is given on any current masthead page.

(12) Experimental procedure for **4**: To a solution of **1** (150 mg, 0.25 mmol) and 5 mL of hexane was added Se metal (100 mg, 1.25 mmol, 5 equiv). The solution was stirred for 10 days at 30 °C. The reaction mixture was filtered and recrystallized from hexane at -78 °C to give **4** as a yellow solid, which was 80% pure by ^{31}P NMR (20% was **1** that could not be removed): yield 89 mg (53%); ^1H NMR (C_6D_6) δ 1.99 (s, 6 H), 2.13 (s, 6 H), 2.33 (s, 12 H), 2.95 (s, 12 H), 6.30 (s, 4 H), 6.80 (s, 4 H); ^{29}Si NMR (INEPT, C_6D_6) δ -11.25 (t, $|^1J_{SiP}| = 29$ Hz); ^{31}P NMR (C_6D_6) δ +146.66 (s, $|^1J_{Si-P}| = 29$ Hz, $|^1J_{Se-P}| = 83$ Hz); ^{77}Se NMR (C_6D_6) δ 64.2 (t, $|^1J_{Se-P}| = 83$ Hz); MS (FD, 3 mA) m/z 672, 674 (^{78}Se, ^{80}Se), (EI) m/z [M - P]$^+$ calcd 641.1892, found 641.1891.

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Cyclopropylcarbene-Tungsten Complexes + Alkynes: A [4 + 2 + 1] Cycloaddition Route for the Construction of Seven-Membered Rings

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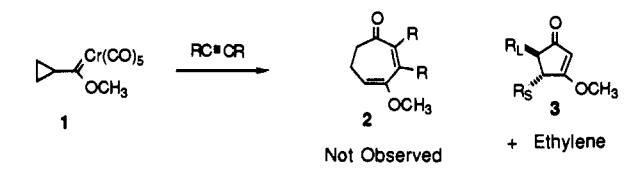
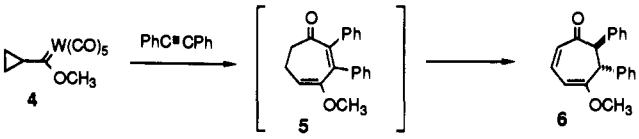
Carbocyclic seven-membered rings are present in a variety of medicinally important compounds and are typically constructed by ring expansion reactions, cyclization reactions, reactions of other seven-membered rings, and occasionally cycloaddition reactions. Cycloaddition reactions have the greatest potential, but few leading to direct formation of a seven-membered ring have been reported.[1] To develop a seven membered ring forming cycloaddition reaction, the reaction between cyclopropylcarbene-chromium complexes and alkynes was examined (Scheme I). This reaction produced not cycloheptadienone **2**, but cyclopentenone **3** plus ethylene.[2] Herein we report initial studies of the reaction of the tungsten analogue of **1** (complex **4**) with alkynes, which leads to the desired cycloheptadienones.[3]

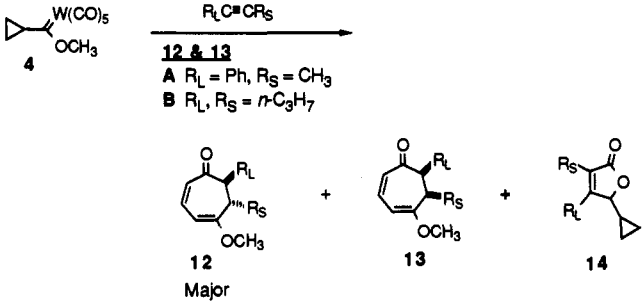
Scheme I



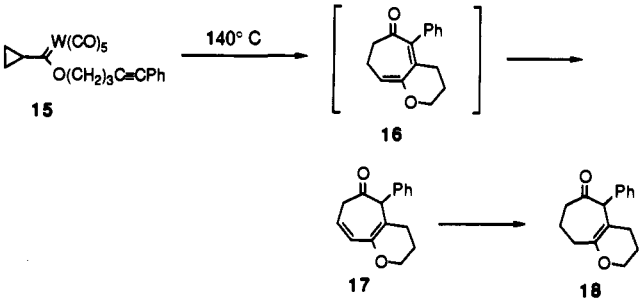
Scheme II



Scheme III



Scheme IV



First, the reaction between diphenylacetylene and tungsten carbene complex **4** was examined. At 100 °C in dioxane, cycloheptadienone derivative **5** was produced in 21% yield along with a trace of rearranged cycloheptadienone **6** (Scheme II). Longer reflux times led to formation of greater amounts of cycloheptadienone **6** at the expense of **5**. Cycloheptadienone **5** was converted to **6** after 2 h at 140 °C; the mechanism presumably involves consecutive 1,5-hydride shifts.[4] In contrast to previous results obtained with alkylcarbene-tungsten complexes and alkynes,[5] the cycloaddition reaction was never complete at 100 °C. Optimal yields of cycloheptadienone **6** (55%) were obtained when the reaction was conducted in refluxing xylene (140 °C) in the presence of 1,2-bis(diphenylphosphino)benzene. Cycloadduct

(1) Some examples of seven-membered ring-forming cycloaddition reactions include the following: (a) Davies, H. M. L.; McAfee, M. J.; Oldenburg, C. E. M. *J. Org. Chem.* **1989**, *54*, 930-936. (b) Noyori, R. *Acc. Chem. Res.* **1979**, *12*, 61-66. (c) Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 1-19. (d) Wulff, W. D.; Yang, D. C.; Murray, C. K. *J. Am. Chem. Soc.* **1988**, *110*, 2653-2655. (e) Trost, B. M.; MacPherson, D. T. *J. Am. Chem. Soc.* **1987**, *109*, 3483-3484. (f) Molander, G. A.; Cameron, K. A. *J. Org. Chem.* **1991**, *56*, 2617-2619. (g) Boger, D. L.; Brotherton, C. E. *J. Org. Chem.* **1985**, *50*, 3425-3427. (h) Harvey, D. F.; Lund, K. P. *J. Am. Chem. Soc.* **1991**, *113*, 5066-5068. (i) Wender, P. A.; Lee, H. Y.; Wilhelm, R. S.; Williams, P. D. *J. Am. Chem. Soc.* **1989**, *111*, 8954-8957.

(2) (a) Herndon, J. W.; Tumer, S. U.; Schnatter, W. F. K. *J. Am. Chem. Soc.* **1988**, *110*, 3334-3335. (b) Herndon, J. W.; Tumer, S. U.; McMullen, L. A.; Matasi, J. J.; Schnatter, W. F. K.; Daitch, C. E. *Comments Inorg. Chem.* **1990**, *10*, 1-24.

(3) (a) Herndon, J. W.; Chatterjee, G.; Patel, P. P.; Matasi, J. J.; Tumer, S. U.; Harp, J. J.; Reid, M. D. *Abstracts of Papers*, 200th National Meeting of the American Chemical Society, Washington, DC; American Chemical Society: Washington, DC, ORGN 101. (b) Herndon, J. W.; Chatterjee, G.; Daitch, C. E. *Abstracts of Papers*, 199th National Meeting of the American Chemical Society, Boston, Massachusetts; American Chemical Society: Washington, DC, 1990; ORGN 13.

(4) ter Borg, A. P.; Kloosterziel, H. *Recl. Trav. Chim. Pays-Bas* **1963**, *82*, 1189-1196.

(5) Macomber, D. W. *Organometallics* **1984**, *3*, 1589-1591.

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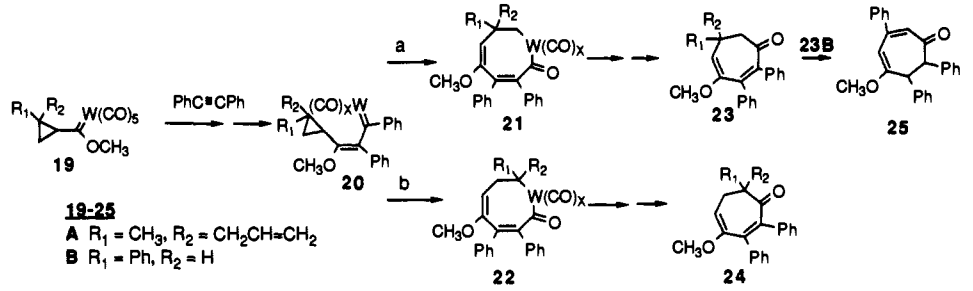
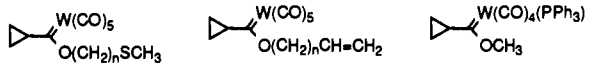
Scheme V



yields were generally higher when triarylphosphines were present in the reaction, but the reaction was severely retarded by more nucleophilic phosphines like (diphenylphosphino)ethane and tributylphosphine. Triphenylphosphine-substituted complex **11** was considerably less reactive than pentacarbonyl complex **4**,[6] suggesting that phosphines assist with some later stage of the reaction, but are detrimental if initial CO-ligand replacement occurs. Contrary to our predictions, complexes **7-10** were as unreactive as the parent carbene complex **4** in reactions with diphenylacetylene.[7]



7 n = 2
8 n = 3

9 n = 2
10 n = 3

11

The reaction proceeded similarly with 4-octyne or 1-phenylpropyne at 140 °C to produce isomerized cycloheptadienone derivatives (**12** + **13**) in 61% (**12A**:**13A** = 85:15) and 45% (only **12B**) yields, respectively (Scheme III). With 1-phenylpropyne, only the indicated regioisomer was obtained.[5,8] In these two cases, substantial amounts of furanones (**14**) were obtained when a phosphine additive was omitted.[9] Terminal alkynes did not provide cycloheptadienone derivatives. Upon thermolysis, alkyne-carbene complex **15** produced cycloheptadienone derivative **17** in 63% yield (Scheme IV). Cycloheptadienone **17** is presumably the thermodynamically more stable compound, perhaps due to an anomeric effect.[10] At long reflux times (>20 h), hydrogenated compound **18** was a significant impurity.

Carbene complexes containing unsymmetrical cyclopropane rings can lead to two possible cycloaddition products (Scheme V). Reaction of diphenylacetylene with complex **19A** led to only cycloheptadienone **23A** in 30% yield; with (phenylcyclopropyl)carbene complex **19B**, cycloheptadienone **25** was produced in 53% yield. The observed regiochemistry reflects a preference for breaking the less-substituted carbon-carbon bond of the cyclopropane ring in the ring-opening step,[2a,11] eventually giving the compound wherein tungsten is bonded to the less-substituted carbon in intermediate metallacycle **21** (path a). The reaction is obviously driven by steric effects since the activating effect of a phenyl ring should have driven the reaction toward pathway b.[13]

In summary, we have discovered a new cycloaddition reaction for the synthesis of seven-membered rings. The reaction shows regioselectivity both in the alkyne addition steps and in the cyclopropane ring opening steps and is a potentially powerful synthetic method. Further investigations in the areas of yield optimization and delineation of the differences in behavior of different cyclopropane-substituted metal-carbene complexes are ongoing.

Acknowledgment. This research was supported by grants from the National Institutes of Health (GM-40777) and the donors of the Petroleum Research Fund, administered by the American Chemical Society (23332-AC1).

Supplementary Material Available: Complete experimental procedures and characterization for all key compounds including ^1H and ^{13}C NMR, IR, and mass spectral data and ^1H and ^{13}C NMR spectra (29 pages). Ordering information is given on any current masthead page.

(6) For *alkyl*carbene-chromium complexes, the triphenylphosphine-substituted complexes are more reactive. Xu, Y.-C.; Wulff, W. D. *J. Org. Chem.* **1987**, *52*, 3263-3275.

(7) For a successful application of this approach, see: Dötz, K. H.; Erben, H.-G.; Harms, K. *J. Chem. Commun.* **1989**, 692-693.

(8) (a) Wulff, W. D.; Tang, P.-C.; McCallum, J. S. *J. Am. Chem. Soc.* **1981**, *103*, 7677-7678. (b) Dötz, K. H.; Dietz, R. *Chem. Ber.* **1977**, *110*, 1555-1563.

(9) Furans and furanones are often byproducts in the reaction between Fischer carbene complexes and alkynes. McCallum, J. S.; Kunng, F. A.; Gilbertson, S. R.; Wulff, W. D. *Organometallics* **1988**, *7*, 2346-2360.

(10) See: Venkataraman, H.; Cha, J. K. *Tetrahedron Lett.* **1989**, *30*, 3510-3513 and references therein.

(11) For a recent reference to mechanistic studies of the reaction between alkynes and Fischer carbene complexes, see: Anderson, B. A.; Wulff, W. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 8615-8617. An alternative mechanistic pathway has been suggested by a reviewer: the reaction produces (cyclopropylvinyl)ketene intermediate, which undergoes electrocyclic ring closure to generate a cycloheptadienone. This mechanism is probably not operative since 4-cyclopropyl-4-methoxy-2,3-diphenyl-2-cyclobutenone and 4-cyclopropyl-4-hydroxy-2,3-diisopropoxy-2-cyclobutenone both fail to produce seven-membered rings upon thermolysis.[12] Metal-complexed vinylketenes, however, cannot be ruled out as intermediates.

(12) For a recent reference to this chemistry, see: Danheiser, R. L.; Brisbois, R. G.; Kowalczyk, J. J.; Miller, R. F. *J. Am. Chem. Soc.* **1990**, *112*, 3093-3110 and references therein.

(13) This is an example of a donor-acceptor-activated cyclopropane, and thus the ring should open as in path b. Reissig, H.-U. *Top. Curr. Chem.* **1988**, *144*, 73-136.

Catalytic Disproportionation of Hydrogen Peroxide by $[Mn^{IV}(\mu_2\text{-}O)(SALPN)]_2$

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Functional modeling of the reactions performed by the manganese catalase and the oxygen evolving complex are scarce although two systems which catalytically convert hydrogen peroxide to dioxygen and water have been described. The first[1] employs a dimanganese Schiff base complex which cycles between Mn^{II}_2 and Mn^{III}_2 while the second[2] uses a Mn(III) porphyrin dimer that may achieve the Mn(IV) or Mn(V) oxidation level during catalysis. Although groundbreaking in their ability to catalyze this important reaction, neither system contains the biologically precedented $(\mu_2\text{-}O^{2-})_2$ core. Previously, models having this structural unit have not exhibited catalase activity.[1] We have described[4] the quantitative formation of $[Mn^{IV}(SALPN)(\mu_2\text{-}O)]_2$ (**1**) by the reaction of [bis(salicylideneaminato)propane][acetonylacetonate]manganese(III), (Mn^{III}(SALPN)(AcAc)) with hy-

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(2) Naruta, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1991**, *113*, 3595-3596.

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(4) Larson, E. J.; Pecoraro, V. L. *J. Am. Chem. Soc.* **1991**, *113*, 3810.

(5) Larson, E. J.; Riggs, P.; Penner-Hahn, J. E.; Pecoraro, V. L. Submitted to *J. Chem. Soc., Chem. Commun.*

(6) Stibrany, R. T.; Gorun, S. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, No. 10, 1156.

(7) Cofré, P.; Sawyer, D. T. *Inorg. Chem.* **1986**, *25*, 2089-2092.

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