ence for vinyl migration.[13] This preference has been ascribed to participation by the $\pi$-system in the transition state for the migration step;[14] perhaps similar factors dictate the insertion regiochemistry in the titanacyclobutenes. Vinyl migration may also be favored by partial development of conjugation in the transition state leading to the vinyl insertion product. Steric factors appear to play a considerable role in directing this chemistry, in at least two regards. If the R and R′ groups (Scheme I) are too large, insertion into the more accessible titanium-alkyl bond is favored.[15] More importantly, once this insertion occurs, the R group on the $\alpha$-carbon of the product metallacycle severely hinders approach to the remaining Ti–C bond, precluding formation of the double-insertion product from the titanium-alkyl single-insertion product. Initial insertion into the titanium-vinyl bond, on the other hand, provides a metallacyclic product that is still quite reactive toward additional nitrile.

We are continuing to explore the generality of these metal-vinyl insertion reactions, their use in the synthesis of heavily substituted pyridine derivatives, and the factors behind the unusual insertion regioselectivity.

**Acknowledgment.** This paper is dedicated to the memory of Professor John K. Stille. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Institutes of Health (Grant No. GM 39494) for the support of this research.

**Supplementary Material Available:** Characterizations and methods of preparation of **2a,b**, **3a,b**, **4a-k**, and **5-7** (11 pages). Ordering information is given on any current masthead page.

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[13] See, e.g.: Pelletier, S. W.; Chang, C. W. J.; Iyer, K. N. *J. Org. Chem.* **1969**, *34*, 3477-3483. Payne, G. B.; Williams, P. H. *Ibid.* **1959**, *24*, 284-286. Walton, H. M. *Ibid.* **1957**, *22*, 1161-1165. Caspi, E.; Shimizu, Y. *Ibid.* **1965**, *30*, 223-226. Velluz, L.; Amiard, G.; Martel, J.; Warnant, J. *Bull. Soc. Chim. Fr.* **1957**, 1484-1489 and references therein.

[14] See, e.g.: Wenkert, E.; Rubin, M. *Nature* **1952**, *170*, 708-709.

[15] To continue the analogy with the Baeyer-Villiger oxidation, similar overrides of intrinsic migratory aptitude by unfavorable steric interactions have been noted: Sauers, R. R.; Ahearn, G. P. *J. Am. Chem. Soc.* **1961**, *83*, 2759-2762. Meinwald, J.; Frauenglass, E. *Ibid.* **1960**, *82*, 5235-5239. Saunders, W. H., Jr. *Ibid.* **1955**, *77*, 4679-4681. Winnik, M. A.; Stoute, V. *Can. J. Chem.* **1973**, *51*, 2788-2793.

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# Manganese Fischer Carbene Chemistry: Reactions of $Cp'(CO)_2Mn{=}C(OMe/OLi)R$ with Enynes, 1-Hexyne, and Acrylates[†]

Thomas R. Hoye* and Gretchen M. Rehberg

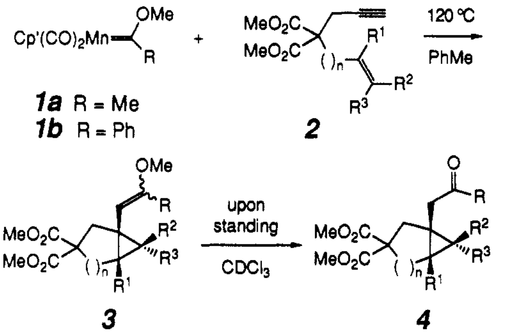
*Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455*

*Received September 17, 1990*

*Summary:* Reactions of the title carbene complexes, both the neutral methoxy (**1a,b**) and anionic "lithoxy" (**1c**) versions, with $\alpha,\omega$-enynes **2** give the bicyclic cyclopropanes **3**. The anion also reacts with 1-hexyne to give the butenolide **5** and with acrylate esters to give the $\gamma$-keto esters **8**.

In 1967 Fischer described[1] the preparation of $Cp'(CO)_2Mn{=}C(OMe)R$ ($Cp' = C_5H_4Me$; R = Me (**1a**), Ph (**1b**)), but the reactivity of these manganese carbene complexes has not been studied.[2] Given our experience in defining the reactivity patterns of a series of related chromium carbene complexes differing in the nature of the donor atom substituent X with several benchmark substrates,[3] we wished to similarly calibrate the reactivity of some non group VI metal based carbenes. Described here are the results of a survey of the reactions of (a) the neutral carbene complexes **1a,b** with enyne substrates **2** (to give the bicyclic cyclopropyl enol ethers **3** and derived ketones **4**), (b) the anionic species **1c** with **2** (to give **3** and then **4**), (c) **1c** with 1-hexyne (to give the butenolide **5**), and (d) **1c** with the acrylate derivatives **7** (to give the keto esters **8**).

(a) The manganese carbene complex **1a** was reacted[4a] with the series of enyne diesters **2a-d** to give the bicyclic vinylcyclopropanes **3a-d** as a mixture of *E* and *Z* enol ethers, which were easily hydrolyzed to the corresponding ketones **4a-d** as previously observed.[3a] It is especially



**2-4**

| | $R^1$ | $R^2$ | $R^3$ | R | *n* | yield of **3** from **2**, % |
|---|---|---|---|---|---|---|
| a | H | H | H | Me | 1 | 71 |
| b | H | H | H | Me | 2 | 63 |
| c | H | H | Me | Me | 1 | (57 of **4** from **2**) |
| d | H | Me | H | Me | 1 | 65 |
| e | H | H | H | Ph | 1 | 68 |

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[†] Dedicated to the memory of Professor John K. Stille and in recognition of his many important contributions to organometallic chemistry.

[1] Fischer, E. O.; Maasböl, A. *Chem. Ber.* **1967**, *100*, 2445.

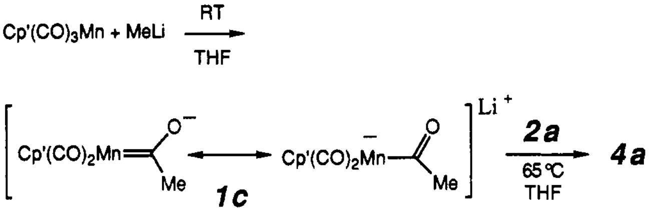
[2] The conversion of 1 (R = $^n$Bu) to $Cp'(CO)(PPh_3)Mn{=}C(OMe)^nBu$, $^n$BuLi-induced formation of $Cp'(CO)(PPh_3)MnC{\equiv}C^nPr$, and subsequent, highly efficient reactions of this anion with a variety of electrophiles was recently reported: Lugan, N.; Kelley, C.; Terry, M. R.; Geoffroy, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 3220.

[3] (a) Korkowski, P. F.; Hoye, T. R.; Rydberg, D. B. *J. Am. Chem. Soc.* **1988**, *110*, 2676. (b) Hoye, T. R.; Rehberg, G. M. *Organometallics* **1989**, *8*, 2070. (c) Hoye, T. R.; Rehberg, G. M. *J. Am. Chem. Soc.* **1990**, *112*, 2841.

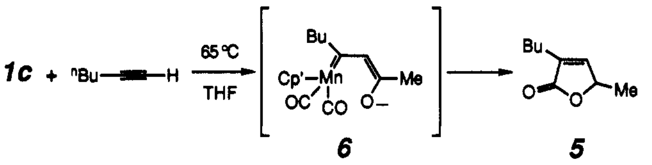
[4] (a) A toluene solution of carbene complex **1a** or **1b** (~0.7 M) and enyne **2** (~1.3 equiv) was placed in a screw-capped culture tube and heated at 120 °C for 5-12 h. The resulting black solution was left open to the air for ~1 h, and the resulting slurry was eluted through a plug of silica gel to remove most of the oxidized, metal-containing byproducts. MPLC of the eluate gave the cyclopropanes **3**, which slowly hydrolyzed[3a] to **4** when exposed to $CDCl_3$ and open to ambient conditions. (b) A THF solution of $Cp'Mn(CO)_3$ (0.7 M) in a nitrogen-flushed flask equipped with a reflux condenser was treated with ethereal MeLi (1.0 equiv) and stirred at room temperature for ~1 h. The substrate [**2a** (1.3 equiv), 1-hexyne (1.5-2.0 equiv), or **7a-c** (1.5-2.0 equiv)] was added to the resulting darkly colored solution, which was then heated in a 65 °C bath for ~12 h. Isolation and purification were the same as described above.

noteworthy that there was no evidence for competing formation of cyclobutanone, furan, or metathesis products, which were observed in reactions of the corresponding chromium complex $(CO)_5Cr{=}C(OMe)Me$ with **2a–d**.[3a] In this regard the manganese complex reacted similarly to (1-pyrrolidinoethylidene)pentacarbonylchromium, which also gave no products from carbonyl insertion and ketene formation with these enynes.[3b] The phenyl-substituted complex **1b**[1] also smoothly reacted[4a] with the enyne **2a** to give the bicyclic vinylcyclopropane **3e**, which underwent hydrolysis to the corresponding ketone **4e**.

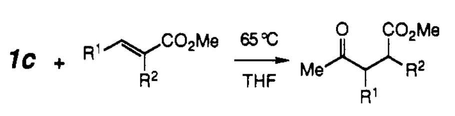
(b) The addition of simple carbanions to chromium hexacarbonyl results in an acyl metalate that may be considered a carbene complex with a particularly rich donor atom. We have recently shown that these anionic species themselves will enter into useful and efficient reactions with the enynes **2** and terminal alkynes.[3c] Reaction of $Cp'(CO)_3Mn$ with methyllithium to generate the manganate species **1c** and subsequent in situ reactions[4b] with the enyne diester **2a** also resulted in the formation of the cyclopropyl ketone **4a** in even higher yield (83%) than with the neutral analogue **1a**.



(c) The in situ reaction[4b] of the manganate anion **1c** with 1-hexyne resulted in the formation of butenolide **5** in 67% yield. This transformation is entirely analogous to that observed for the acylpentacarbonylchromate species, and we have previously proposed mechanistic pathways analogous to that by which the presumed vinylogous acylmetalate **6** might lead to **5**.[3c]



(d) The reaction[4b] of the manganate **1c** with the α,β-unsaturated esters **7a–c** resulted in the formation of the γ-keto esters **8a–c**, which are formally products of the addition of an acetyl anion in a Michael fashion to the enoates. This event is reminiscent of reactions of the nickel acylate species generated by addition of alkyllithium species to nickel tetracarbonyl.[5] We have observed this and related reaction types with the corresponding acylchromate species as well.[6]



**7** **8**

| | $R^1$ | $R^2$ | yield, % | |
|---|---|---|---|---|
| **7a** | H | H | 79 | **8a** |
| **7b** | Me | H | 68 | **8b** |
| **7c** | H | Me | 61 | **8c** |

The use of the neutral manganese carbene complexes **1a** and **1b** allows for a more economical[7] and environmentally acceptable access to some of the typical reaction pathways that have been previously demonstrated for the analogous chromium carbene complexes. In addition the chemistry of the anionic manganate **1c** further demonstrates the utility of these in situ generated "carbenes". The operational ease and convenience associated with this one-flask procedure, which avoids the necessity of isolating or handling the metal carbene complex, makes the use of these anions quite attractive and leads us to strongly recommend the use of this in situ methodology.

**Acknowledgment.** This investigation was supported by Grant GM-38854 awarded by the DHHS and by an award from the Alfred P. Sloan Foundation.

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(5) Corey, E. J.; Hegedus, L. S. *J. Am. Chem. Soc.* **1969**, *81*, 4926.

(6) Hoye, T. R.; Rehberg, G. M. Manuscript in preparation.

(7) $Cp'Mn(CO)_3$ is currently nearly 1 order of magnitude less expensive (Johnson Matthey/Alfa) than $Cr(CO)_6$ on the basis of the molar equivalents of utilized CO ligands.

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# Synthesis, Structure, and Reactivity of an Organogermanium Lewis Acid

Scott E. Denmark,* Robert T. Jacobs, Ginny Dai-Ho, and Scott Wilson†

*Roger Adams Laboratory, Department of Chemistry, University of Illinois, Urbana, Illinois 61801*

*Received September 14, 1990*

*Summary:* The 8-Ge-4 spirogermanacycle **3** was prepared from hexafluorocumyl alcohol and its structure determined by X-ray crystallography. The distortion of the internal O–Ge–C angles leads to an enhanced Lewis acidity, which was illustrated by the promotion of pericyclic reactions involving activation of aldehyde carbonyl groups. Four 10-Ge-5 anionic complexes were prepared, and X-ray crystallographic analysis of the *n*-butyl adduct **4b** showed a trigonal-bipyramidal geometry.

The development and application of chiral Lewis acids as catalysts and promoters of organic reactions have dramatically increased in recent years. The majority of these highly specialized reagents is based on a limited set of central elements from the main-group (B,[1] Al,[2] Sn[3]), transition (Ti,[4] Zn,[5] Ru,[6] W,[7] Re[8]), and even lanthanide

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† To whom correspondence concerning the structure determinations should be directed.

(1) (a) Furuta, K.; Shimizu, S.; Miwa, Y.; Yamamoto, H. *J. Org. Chem.* **1989**, *54*, 1481. (b) Furuta, K.; Kanematsu, A.; Yamamoto, H. *Tetrahedron Lett.* **1989**, *30*, 7231. (c) Furuta, K.; Miwa, Y.; Iwanaga, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 6254. (d) Kelly, T. R.; Whiting, A.; Chandrakumar, N. S. *Ibid.* **1986**, *108*, 3510. (e) Bir, G.; Kaufmann, D. *Tetrahedron Lett.* **1987**, *28*, 777.

(2) (a) Takemura, H.; Komeshima, N.; Takahashi, I.; Hashimoto, S.; Ikota, N.; Tomioka, K.; Koga, K. *Tetrahedron Lett.* **1987**, *28*, 5687. (b) Maruoka, K.; Itoh, T.; Shirasaka, T.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 310. (c) Chapuis, C.; Jurczak, J. *Helv. Chim. Acta* **1987**, *70*, 436. (d) Corey, E. J.; Imwinkelried, R.; Pikul, S.; Xiang, Y. B. *J. Am. Chem. Soc.* **1989**, *111*, 5493.

(3) (a) Krishnamurti, R.; Kuivila, H. G. *J. Org. Chem.* **1986**, *51*, 4947. (b) Mukaiyama, T.; Kobayashi, S.; Sano, T. *Tetrahedron* **1990**, *46*, 4653.

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