to their diequatorial isomers.[10] However, these latter reactions proceed through a tight ion pair, while the rearrangements reported here appear to proceed through either a relatively loose ion pair intermediate 8 or by reversion of the product to its ionic reactants. The results of experiments summarized below do not at present allow a clear choice to be made between these alternatives.

The relative rates of addition of phthalimide and of 4-nitrophthalimide to 2 were determined by competition experiments and found to be 2.0:1.0.[11] When the rearrangement of **4a** was allowed to proceed at room temperature in the presence of 2 M equiv of lithium 4-nitrophthalimide, the product was found to be a 4.0:3.0 mixture of the rearranged complexes **6a** and **6d**, consistent with incomplete exchange of anions in an ion pair such as 8. However, rearrangement of **4a** in the presence of a 2:1 molar ratio of 4-nitrophthalimide to **4a** led to the exclusive formation of **6d**, suggesting that, if an ion pair intermediate is involved in the rearrangement, proton exchange between the migrating phthalimide anion and the more acidic 4-nitrophthalimide must be faster than rearrangement of the ion pair.[12]

Regardless of the precise nature of the intermediate in these reactions, stereoelectronic factors would be expected to require that the rearrangement proceed through that conformer in which the addend substituents are axial. The faster rates of rearrangement of **5a**–**5c**, compared with the corresponding **4a**–**4c** adducts, are in accord with that expectation.[13]

Finally, it is of interest to note that adducts 4, derived from the addition of acetyl acetonate and dimethyl malonate anions to 2, do not undergo dyotropic rearrangement even on prolonged heating at 40 °C in THF and even though these adducts exist predominantly in the diaxial form. Anion stability alone cannot therefore be a determining factor in promoting dyotropic rearrangement. Instead, these observations find a plausible explanation in terms of an anomeric effect,[14] which promotes adduct reversion through a weakening of the carbon–heteroatom bond in 4 and 5.

Further work in progress is designed to apply these reactions to the synthesis of either of two enantiomeric 3-hydroxy esters starting from a single homochiral dioxene complex.

Acknowledgment. This work was supported by a grant from the National Institutes of Health (GM-37067). We thank K. Wheeler for assistance with the X-ray structure determination.

Supplementary Material Available: Experimental procedure and tables of unimolecular rate constants, crystallographic data, atomic coordinates, bond lengths and angles, and thermal parameters for **4a** and **6a** (31 pages); tables listing calculated and observed structure factors for **4a** and **6a** (22 pages). Ordering information is given on any current masthead page.

---

[10] Barton, D. H. R.; Head, A. J. *J. Chem. Soc.* **1956**, 932. Grob, C. A.; Winstein, S. *Helv. Chim. Acta* **1952**, *35*, 782.

[11] An equimolar mixture of the two salts, generated at low temperature by treatment of the imides with *n*-butyllithium, were allowed to react with a half molar equivalent of 2 in THF solution. The initial product, a mixture of **4a**, **6a**, and **6d**, was allowed to equilibrate further at room temperature to yield a mixture of **6a** and **6d** in a ratio of 2.0 ± 0.1:1.0, determined by separated integration of proton resonances at the three methine center in **6a** and **6d**.

[12] The pK_a's of phthalimide and 4-nitrophthalimide in 30% aqueous ethanol at 25 °C are 10.02 and 8.55, respectively. Guérillot, C. R. *C. R. Hebd. Seances Acad. Sci.* **1955**, *240*, 1107.

[13] The difference in populations of the diaxial addend conformations in 5 and 4 and the corresponding rearrangement rate differences are due to the higher energy of the diequatorial addend conformation in 5 compared with this conformer in 4. These should differ by approximately 0.64 kcal/mol, the energy of an axial methyl group in a 1,4-dioxane. Ayras, P.; Nikkila, A.; Nurmi, T.; Pihlaja, K. *Finn. Chem. Lett.* **1974**, 237.

[14] Kirby, A. J. *The Anomeric Effect and Related Stereoelectronic Effects At Oxygen*; Springer Verlag: Berlin, 1983.

Metal–Vinyl vs Metal–Alkyl Insertion Reactions of Titanacyclobutenes with Nitriles

Kenneth M. Doxsee* and John K. M. Mouser

Department of Chemistry, University of Oregon, Eugene, Oregon 97403

Received September 13, 1990

Summary: Disubstituted titanacyclobutenes, $Cp_2\overline{TiCR{=}CRCH_2}$ (**1a**, R = CH_3; **1b**, R = CH_2CH_3), react with 2 equiv of nitriles under mild conditions to afford diazatitanacyclooctatrienes, resulting from nitrile insertion into both the titanium–alkyl and titanium–vinyl bonds of the titanacyclobutene. Hydrochlorination of these metallacyclic products affords tetrasubstituted pyridines. Significant steric bulk in either the nitrile or the metallacyclobutene leads to exclusive formation of single-insertion products.

Insertion reactions of transition-metal–alkyl bonds are well established.[1] In contrast, insertions into transition-metal–vinyl bonds are rather scarce, being found predominantly for strained metallacyclopropenes[2,3] (alkyne complexes) with the early transition metals, though also occasionally appearing for early and later metal vinyl complexes.[4] In our continuing survey of the reactivity of titanacyclobutenes with unsaturated organic substrates, we have found that insertion into the titanium–vinyl bond is apparently intrinsically favored over the anticipated insertion into the titanium–alkyl bond of the metallacycle,

---

[1] (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 6. (b) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Interscience: New York, 1988; Chapter 27.

[2] Reviews: (a) Bennett, M. A.; Schwemlein, H. P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1296–1320. (b) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047–1058. (c) Erker, G. *J. Organomet. Chem.* **1977**, *134*, 189–202 and references therein.

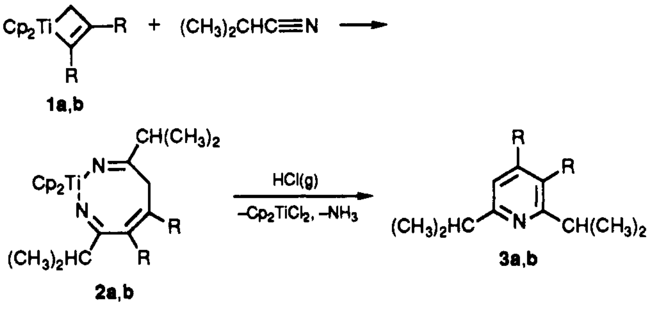
[3] (a) Vaughan, G. A.; Hillhouse, G. L.; Lum, R. T.; Buchwald, S. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 7215–7217. (b) Buchwald, S. L.; Lum, R. T.; Dewan, J. C. *Ibid.* **1986**, *108*, 7441–7442. (c) Buchwald, S. L.; Wannamaker, M. W.; Watson, B. T. *Ibid.* **1989**, *111*, 776–767. (d) Jordan, R. F.; Taylor, D. F. *Ibid.* **1989**, *111*, 778–779.

[4] See, e.g.: Cassar, L.; Giarrusso, A. *Gazz. Chim. Ital.* **1973**, *103*, 793–795; *Chem. Abstr.* **1974**, *81*, 63045 m. Tohda, Y.; Sonogashira, K.; Hagihara, N. *J. Chem. Soc., Chem. Commun.* **1975**, 54. Roe, D. M.; Calvo, C.; Krishnamachari, N.; Moseley, K.; Maitlis, P. M. *Ibid.* **1973**, 436. Dema, A. C.; Lukehart, C. M.; McPhail, A. T.; McPhail, D. R. *J. Am. Chem. Soc.* **1989**, *111*, 7615–7616. Erker, G.; Schlund, R.; Kruger, C. *Organometallics* **1989**, *8*, 2349–2355.

0276-7333/90/2309-3012$02.50/0 © 1990 American Chemical Society

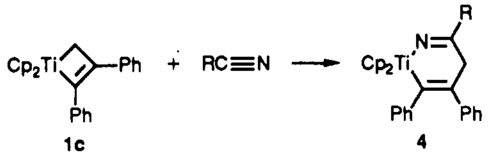
with alkyl insertion observed only in cases where vinyl insertion is sterically disfavored.

Titanacyclobutenes[5] **1a,b** react cleanly[6] with 2 equiv of isobutyronitrile to afford the double-insertion products **2a,b**.[7,8] Addition of dry HCl to solutions of these complexes precipitates Cp_2TiCl_2 and affords the tetrasubstituted pyridine derivatives **3a** (68%)[9] and **3b** (69%).[6] (The pyridines are presumably formed through acid-catalyzed cyclization of the diimine anticipated as the initial product of the hydrochlorination.)



a, R = CH_3; **b**, R = CH_2CH_3

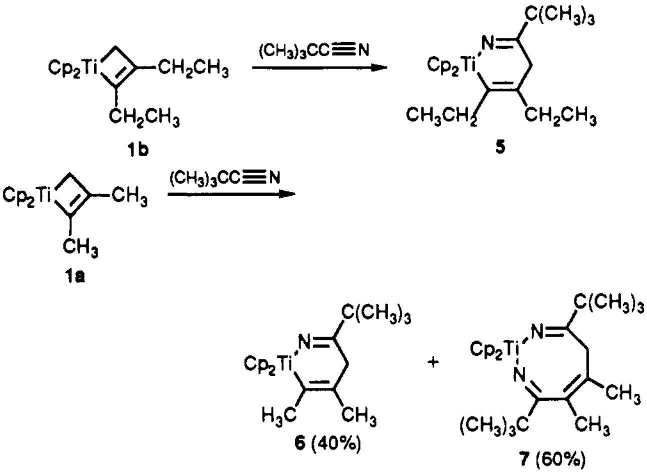
In contrast, the diphenyltitanacyclobutene **1c** reacts readily with a wide variety of nitriles to afford *single*-insertion products, **4**, characterized by ^1H and ^{13}C NMR spectroscopy and high-resolution mass spectroscopy.[6]



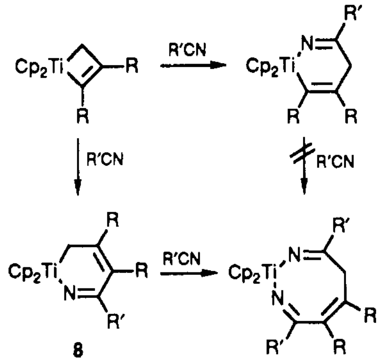
a, R = CH_3; **b**, R = CH_3CH_2; **c**, R = $(CH_3)_2CH$; **d**, R = $(CH_3)_3C$; **e**, R = C_6H_5; **f**, R = p-F-C_6H_4; **g**, R = p-CH_3O-C_6H_4; **h**, R = p-CH_3-C_6H_4; **i**, R = o-CH_3-C_6H_4; **j**, R = p-CF_3-C_6H_4; **k**, R = C_6F_5

Confirmation of the connectivity of complexes **4** is provided by their hydrolysis to the anticipated β,γ-unsaturated ketones upon treatment with HCl and H_2O.[6] Though we have not examined these reactions mechanistically, complexes **4** presumably form through simple insertion of the nitrile into the titanium–alkyl bond of **1c**.[10]

The diethyltitanacyclobutene **1b** reacts with excess pivalonitrile to afford the analogous single-insertion product **5**, while the dimethyltitanacyclobutene **1a** yields a 2:3 mixture of the single-and double-insertion products **6** and **7**. This mixture of **6** and **7** remains unchanged even after prolonged heating and addition of excess pivalonitrile, suggesting that **6** cannot be converted to **7** under these conditions.



Scheme I



Similarly, **5** will not react with excess isobutyronitrile to form a double-insertion product, though the anticipated product would appear only negligibly more sterically congested than complex **2b**. Apparently, formation of the single-insertion product, such as **5** or **6**, is a dead end as far as formation of the double-insertion products. This suggests that double-insertion products must arise from initial insertion into the titanium-*vinyl* bond, forming complexes such as **8**, which then undergo rapid insertion of a second equivalent of nitrile (Scheme I). Though we have not isolated complexes corresponding to **8**, intermediates do form in the course of the double-insertion reactions that display spectral properties consistent with this proposed structure.[6]

The unreactivity of the metal–vinyl bond has generally been ascribed to stabilizing π-bonding interactions.[11] In the titanacyclobutenes, however, no metal orbitals of proper symmetry and reasonable energy are available for π-interaction with the C=C double bond.[12] Thus, the two Ti—C bonds in the titanacyclobutenes are probably of more similar energy than might have been anticipated, and insertion into the titanium–vinyl bond should not be too surprising. Interestingly, the Baeyer–Villiger oxidation of α,β-unsaturated ketones also appears to display a prefer-

---

(5) Preparation of titanacyclobutenes: (a) Tebbe, F. N.; Parshall, G. W.; Ovenall, D. W. *J. Am. Chem. Soc.* **1979**, *101*, 5074–5075. (b) Tebbe, F. N.; Harlow, R. L. *Ibid.* **1980**, *102*, 6149–6151. (c) Tebbe, F. N.; Parshall, R. L.; Reddy, G. S. *Ibid.* **1978**, *100*, 3611–3613.

(6) Experimental details and characterizations of all new compounds are provided in the supplementary material.

(7) Double-insertion reactions have previously been observed for strained metallacycles and for metallacycles bearing two alkyl groups on the metal. See, e.g.: (a) Buchwald, S. L.; Fisher, R. A. *Organometallics* **1990**, *9*, 871–873. (b) Erker, G.; Humphrey, M. G. *J. Organomet. Chem.* **1989**, *378*, 163–169. (c) Bickelhaupt, F.; Seetz, J. W. F. L.; Van De Heisteeg, B. J. J.; Schat, G.; Akkerman, O. S. *J. Mol. Catal.* **1985**, *28*, 71–83. (d) Yasuda, H.; Okamoto, T.; Matsuoka, Y.; Nakamura, A.; Kai, Y.; Kanehisa, N.; Kasai, N. *Organometallics* **1989**, *8*, 1139–1152 and references therein.

(8) Sequential reactions of a zirconocene derivative with 2 equiv of nitrile were recently reported. In this case, the second equivalent of nitrile inserts into a Zr–N bond of the first-formed metallacycle. Carney, M. J.; Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 8751–8753.

(9) Balaban, A. T.; Balaban, T. S.; Uncuta, C.; Gheorghiu, M. D. *Tetrahedron Lett.* **1985**, 4669–4672.

(10) While this work was in progress, an analogous single-insertion reaction of **1c** was reported: Meinhart, J. D.; Grubbs, R. H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 171–180. No double-insertion products are presented in this report. We find that the facile decomposition reported by these authors for the single-insertion product may be avoided if traces of reducing impurities are *rigorously* excluded. Vacuum distillation of solvents from Na/benzophenone appears to carry over sufficient quantities of reducing agents to destroy the products; atmospheric pressure distillation from Na/K appears preferable. Products derived from **1a,b** are much less prone to decomposition.

(11) Tanke, R. S.; Crabtree, R. H. *Inorg. Chem.* **1989**, *28*, 3444–3447.

(12) Eisenstein, O.; Hoffmann, R.; Rossi, A. *J. Am. Chem. Soc.* **1981**, *103*, 5582–5584. McKinney, R. J.; Tulip, T. H.; Thorn, D. L.; Coolbaugh, T. S.; Tebbe, F. N. *Ibid.* **1981**, *103*, 5584–5586. Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103–109.

ence for vinyl migration.[13] This preference has been ascribed to participation by the π-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 α-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.

---

(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.

Manganese Fischer Carbene Chemistry: Reactions of Cp′(CO)$_2$Mn=C(OMe/OLi)R with Enynes, 1-Hexyne, and Acrylates[†]

Thomas R. Hoye* and Gretchen M. Rehberg

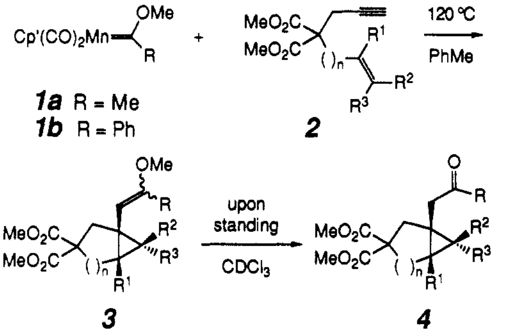
Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Received September 17, 1990

Summary: Reactions of the title carbene complexes, both the neutral methoxy (**1a**,**b**) and anionic "lithoxy" (**1c**) versions, with α,ω-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 γ-keto esters **8**.

In 1967 Fischer described[1] the preparation of Cp′(CO)$_2$Mn=C(OMe)R (Cp′ = C$_5$H$_4$Me; 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

[†] 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)^{n}Bu, ^{n}BuLi-induced formation of Cp′(CO)(PPh$_3$)MnC≡C^{n}Pr, 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.