hexane, the result of endo cyclization, was not observed. An alternate method of ligand removal involved the treatment of the reaction mixture with 1.5 equiv of pyridine, to neutralize the $EtAlCl_2$, followed by addition of 3.0 equiv of *N*-bromosuccinimide. Formation of (bromomethyl)cyclopentane in 94% yield demonstrated the efficient functionalization of the organic ligand following ring formation.

This investigation was extended to the study of vicinally and geminally disubstituted alkenes tethered to titanium (Table I). In general, these complexes were prepared with less than 1% ligand cyclization, and 2 equiv of $EtAlCl_2$ with longer reaction times than those necessary for **3a** was required to obtain >97% ring formation. Although cyclization of **3b** was 99% complete after 2 h at −78 °C, **3c** had progressed to only 65% cyclization under these conditions and required an additional 2.5 h at 23 °C to reach completion.[13] Insertion of a cyclopentene ring into the Ti–C bond proceeded well (**3d** to **4d**), but the tethered cyclohexene substrate **3e** failed to cyclize. In each case, the product ratios obtained for activation of substrates **3a**–**3e** were the same as those observed for free-radical intermediates generated from **1a**–**1e**. Substrates containing geminally disubstituted olefins resulted in selective formation of quaternary carbon centers. The methyl-substituted substrates **3f** and **3i** resulted in the formation of geminal dimethylcyclopentanes following protonolysis,[14] while the exo methylene ring substrates **3g** and **3h** selectively produced cis-fused ring systems with an angular methyl group.[15]

A notable feature of this titanium-mediated cyclization was the selective cyclopentane ring formation, especially in the generation of quaternary centers. These selectivities were similar to those produced by anionic cyclization, in which substrates **g** and **h** (X = Li) produced only exo cyclization products in 80% and 95% conversion, respectively.[16] On the other hand, the significant preference for five-membered-ring products under the titanium/aluminum Ziegler-Natta conditions was opposite those observed for the relatively nonselective free-radical cyclization of substrates **f**–**i**.[17] The high regioselectivities of these metal-mediated cyclizations are due to conformational restrictions on the intramolecular syn coplanar addition of the metal–carbon bond to the olefin.

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(12) Yields for these volatile compounds were determined by capillary GLC analysis of the quenched reaction mixture (HCl/MeOH) using internal standards and correction for detector response. Product confirmation was made by comparison with commercial or independently prepared samples.

(13) These observations were in accord with *Z* and *E* olefin reactivity with zirconocene chloride hydride.[5]

(14) Cyclization of **3i** required a reaction temperature of 80 °C to give optimum results.

(15) In each case, formation of the trans-fused product was not observed for the titanium-mediated or radical cyclization reactions of **3h** or **1h**, respectively.

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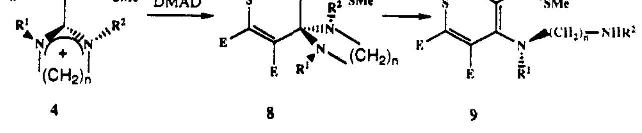
Additions and Corrections

The Chemistry of Enones. Parts 1 and 2. Book Review. [*J. Am. Chem. Soc.* **1990**, *112*, 4095]. SAUL PATAI and ZVI RAPPOPORT

The indexes are in Part 2, not in Part 1 as stated.

From Twisted to Folded Ethylenes [*J. Am. Chem. Soc.* **1988**, *110*, 4843–4844]. AGHA ZUL-QARNAIN KHAN and JAN SANDSTRÖM*

The compounds formed on addition of the 1-thioacyl-2,2-diaminoethylenes **4** to DMAD and claimed to be "folded" ethylenes with pyramidal carbon atoms (**6**) have been shown to be instead 4-aminothiopyrans **9**, formed by ring-opening on workup of the initially formed thiopyran-4-spiro-2′-1′,3′-diazacyclanes **8**.[1]



4 **8** **9**

Compounds **8** were not observed in the initial experiments, since they are transformed to **9** on TLC analysis and chromatographic workup. The structures of analogues of **8** have been determined by X-ray crystallography.[2]

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(2) Khan, Agha Z.; Sandström, J.; Bergquist, K.-E.; Cheng, C.-Y.; Wang, S.-L. *J. Org. Chem.* Accepted for publication.