II). We concluded that the sixth and seventh MOs consisting predominantly of the N(1s) and C(1s) AOs are crucial for the relative stability of the SeFA tautomer. As is evident from the presented data, its relative energy decreases monotonically upon increasing the number of MOs included in the MP2 calculations; however, inclusion of the sixth and seventh MOs drops the ΔE^{MP2} energy from +27.7 to -20.8 kJ/mol.

As one can see, the electron correlation effects are essential in prediction of the relative electronic energies of the studied selenium compounds, and some trends are evident (the shift of the **1** ⇄ **2** equilibrium upon oxygen substitution by sulfur and selenium). In this respect, the present study is the first example of ab initio quantum-mechanical calculations at the electron correlation level that noticed and explained unexpected properties of selenium in systems that mimic simple units of biologically important structures. The predicted differences in the tautomeric equilibria of selenoformamide compared with oxo- and thioformamide might be of importance in explanations of the role of the selenium atom in such biological systems as, for example, selenoproteins.

The following important conclusions emerge from this investigation:

1. Contrary to the formamide and thioformamide cases, the selenoformimidic acid (SeFA) is the lowest energy species. Predicted energy differences (Table I) suggests that SeFA should be observed in the gas phase and/or inert gas matrices, and perhaps this form should exist exclusively in neutral environments.

2. The calculated dipole moments of SeF and SeFA (4.43 and 1.48 D, respectively) show that the tautomeric equilibrium between SeF and SeFA should be shifted toward SeF on going from the gas phase to a polar medium.

3. As is evident from the presented data, the theoretical studies of tautomeric (isomeric) equilibria of the systems involving fourth-row (or heavier) elements should be carried out at the correlated level including both valence and core electrons. It seems that when MP4(full) calculations are not affordable, it is more appropriate to compare MP2(full) rather than MP4(fc) relative energies.

Acknowledgment. We gratefully acknowledge Grant DAAL03-89-0038 from the Army High Performance Computing Research Center. We also thank the Mississippi Center for Supercomputing for an allotment of computer time for the calculations presented here.

Supplementary Material Available: Table III containing calculated molecular parameters including bond lengths and bond angles, dipole moments, rotational constants, and SCF and MP2 energies for selenoformamide and selenoformimidic acid (1 page). Ordering information is given on any current masthead page.

Apparent Endo-Mode Cyclic Carbopalladation with Inversion of Alkene Configuration via Exo-Mode Cyclization–Cyclopropanation–Rearrangement

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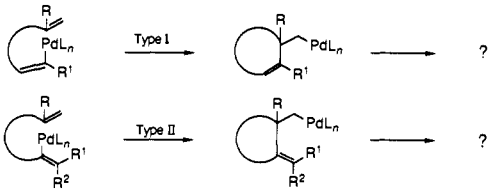
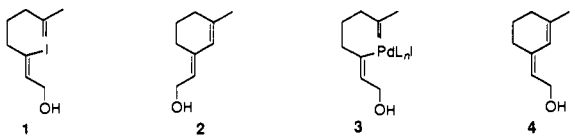
We recently documented what appeared to be the first reported example of cyclopropanation of neopentyl-type alkylpalladium species.[1,2] Since it could compete with common ring formation in cases where cascade carbopalladation[3] involves the addition of alkenylpalladium species to 1,1-disubstituted alkenes, we undertook to dilineate its scope. The cyclic versions of the process mentioned above may be classified into the two types shown in Scheme I, according to the substrate structure. The exo-mode cyclization process is arbitrarily shown.

Scheme I



As the results summarized in Scheme II indicate, cyclopropanation via carbopalladation of neopentyl-type alkylpalladium species appears to be a generally observable process with the type I substrates in the absence of a faster or competitive process, such as common ring formation, provided that there is a β-hydrogen syn-coplanar with Pd in the putative (cyclopropylcarbinyl)palladium intermediates.

In sharp contrast, the type II reaction has predominantly yielded apparent endo-mode cyclization products. Typically, treatment of **1**[4] with 3% of $PdCl_2(PPh_3)_2$, 20% of Et_2NH, and NEt_3 in DMF at 80 °C for 8 h provided **2**[5] in 69% yield. It is significant to note that the reaction proceeded with complete inversion of the alkene configuration. The stereochemistry of **2** was established by ^1H 2D NOESY NMR spectroscopy. Consequently, a mechanism involving a straightforward endo-mode carbopalladation of **3** to give **4** must be ruled out. Such a process would proceed with retention of alkene configuration.



1 2 3 4

More consistent not only with the observed stereochemistry but also with the results of the type I cyclization reactions is a sequence involving (i) exo-mode carbopalladation, (ii) cyclopropanation, and (iii) cyclopropylcarbinyl-to-homoallyl rearrangement (Scheme III). We believe that the experimental results and literature information presented below fully support this mechanism, which unifies the mechanisms of the type I and type II reactions.

Since the plausibility of the mechanism shown in Scheme III critically hinges on the stereochemistry of the reaction, all products containing a stereodefined exocyclic alkene moiety have been subjected to ^1H 2D NOESY NMR spectroscopic analysis. All such products, i.e., **2** and **5–9**,[5] yielded NMR spectroscopic data confirming inversion of alkene configuration shown in Scheme III. The *E* configuration of **5** was further established by X-ray analysis of its *p*-nitrobenzoate. Conversion of **10**[4] into **5** in 68% yield was carried out as that of **1** into **2**. The same procedure was also satisfactory for converting **11**[6] into **6** in 94% yield, while the reaction of enynes, e.g., **12**[7] and **13**,[7] with organic halides, e.g., PhI and α-bromostyrene, catalyzed by Pd–phosphine complexes, e.g., $Pd(PPh_3)_4$, provides a convenient procedure for the type II

(1) Zhang, Y.; Negishi, E. *J. Am. Chem. Soc.* **1989**, *111*, 3454.

(2) For subsequent reports on this subject, see: (a) Grigg, R.; Dorrity, M. J.; Malone, J. F.; Sridharan, V.; Sukirthalingam, S. *Tetrahedron Lett.* **1990**, *31*, 1343. (b) Grigg, R.; Sridharan, V.; Sukirthalingam, S. *Tetrahedron Lett.* **1991**, *32*, 3855. (c) Meyer, F. E.; Parsons, P. J.; de Meijere, A. *J. Org. Chem.* **1991**, *56*, 6487. For a related cyclobutanation, see: Carpenter, N. E.; Kucera, D. J.; Overman, L. E. *J. Org. Chem.* **1989**, *54*, 5896.

(3) For a review, see: Negishi, E. *Pure Appl. Chem.* **1992**, *64*, 323. See also: Zhang, Y.; Wu, G.; Agnel, G.; Negishi, E. *J. Am. Chem. Soc.* **1990**, *112*, 8590.

(4) Prepared by treatment of the corresponding propargyl alcohols with $LiAlH_4$ and NaOMe followed by iodinolysis (Corey, E. J.; Katzenellenbogen, J. A.; Posner, G. H. *J. Am. Chem. Soc.* **1967**, *89*, 4245).

(5) All cyclization products have been identified by spectroscopic methods including high-resolution mass spectroscopy.

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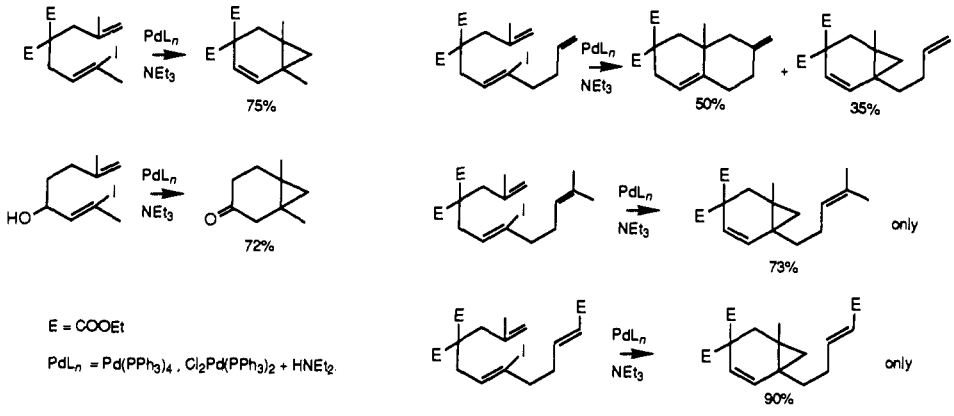
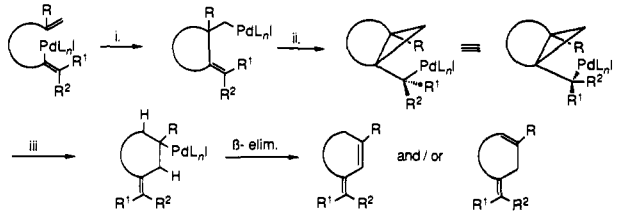
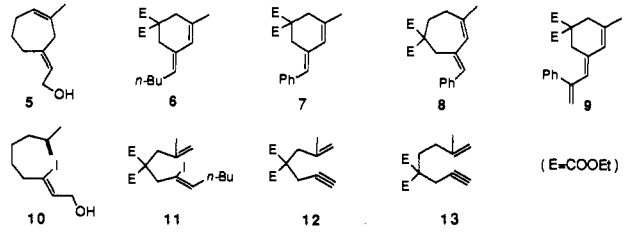
Scheme II



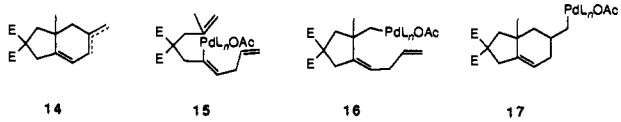
Scheme III



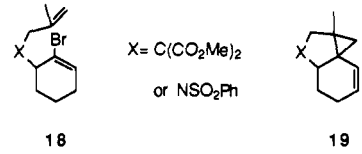
reaction.[8] This procedure was indeed used for conversion of **12** into **7** (52%) and **9** (54%) as well as that of **13** into **8** (59%) in the yields shown in parentheses.



That the initial step in the type II reactions reported here must involve exo-mode, rather than endo-mode, carbopalladation has been indicated by the reaction of **12** with allyl acetate catalyzed by $Pd(PPh_3)_4$ to give **14**[5] in 48% yield (exo/endo = 2/1). The reaction must have proceeded via **15–17**.



In none of the type II reactions presented above was there any direct evidence for the formation of cyclopropyl derivatives. This is true even with those cases where the putative (cyclopropylcarbinyl)palladium intermediates can undergo dehydropalladation, such as the reactions of **10** and **11**. To date, the only known example which amounts to trapping of (cyclopropylcarbinyl)palladium species in the type II reaction is the Pd-catalyzed conversion of **18** into **19** reported by Grigg et al.[2b] It is reasonable to assume that the well-documented cyclopropylcarbinyl-to-homoallyl rearrangement[9] or its reversal[1,2] requires the syn-coplanar arrangement of the C–Pd bond and the participating C–C bond of cyclopropanes. On this basis, if (cyclopropylcarbinyl)palladium species are structurally rigid, the only allowed cyclopropylcarbinyl-to-homoallyl rearrangement may be the reversal of cyclopropanation. Under such conditions, vinylcyclopropanes, e.g., those shown in Scheme II and **19**, may be obtained as products. On the other hand, if (cyclopropylcarbinyl)palladium



species are conformationally flexible, the C–Pd bond can be syn-coplanar with the C–C bond between the two bridgehead carbon atoms of the bicyclo[*n*.1.0] system, permitting ring expansion via rearrangement. The overall transformation then amounts to an apparent endo-mode cyclization with inversion of alkene configuration. We have thus far identified just two examples of the apparent endo-mode carbopalladation reactions of alkenylpalladium species in the literature.[10] These results are entirely consistent with the mechanism proposed above. In conclusion, this study has not only delineated the scope of the type I and type II cyclization reactions but also provided a unifying mechanism for seemingly unrelated processes in these reactions.

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Supplementary Material Available: Listings of spectral data for the compounds mentioned in the text (5 pages). Ordering information is given on any current masthead page.

(6) Prepared by the base-promoted reaction of diethyl methallylmalonate with (*Z*)-2-iodo-2-heptenyl mesylate which, in turn, was prepared via successive treatment of the corresponding propargyl alcohol with *n*-BuLi, *i*-Bu_2AlH, and I_2 (Corey, E. J.; Kirst, H. A.; Katzenellenbogen, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 6314).

(7) Prepared by allylation or homoallylation followed by propargylation of diethyl malonate.

(8) For related cyclization reactions initiated by external halides and related derivatives, see: (a) Negishi, E.; Harring, L. S.; Owczarczyk, Z.; Mohamud, M. M. *Tetrahedron Lett.* **1992**, *33*, 3253. (b) Trost, B. M.; Pfrengle, W.; Urabe, H.; Dumas, J. *J. Am. Chem. Soc.* **1992**, *114*, 1923. (c) Trost, B. M.; Dumas, J. *J. Am. Chem. Soc.* **1992**, *114*, 1924.

(9) (a) Green, M.; Hughes, R. P. *J. Chem. Soc., Dalton Trans.* **1976**, 1880. (b) Larock, R. C.; Varaprath, S. *J. Org. Chem.* **1984**, *49*, 3432. (c) Donaldson, W. A.; Brodt, C. A. *J. Organomet. Chem.* **1987**, *330*, C33.

(10) (a) Grigg, R.; Coulter, T. *Tetrahedron Lett.* **1991**, *32*, 1359. (b) Gaudin, J. M. *Tetrahedron Lett.* **1991**, *32*, 6113.