products and other synthetic impurities.[15]

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Registry No. [^3H]Ac-Ala-Phe-Cys(H)-NH_2, 127279-51-0; Ac-Tyr-Gly-Cys(H)-NH_2, 127279-52-1; (Ac-Tyr-Gly-Cys-NH_2)$_2$ (disulfide linkage), 127279-53-2; [^3H]Ac-Ala-Phe-Cys-NH_2, Ac-Tyr-Gly-Cys-NH_2 (disulfide linkage), 127258-03-1; $HSCH_2COOH$, 68-11-1; 2-HSC_6H_4COOH, 147-93-3; 2-(NO_2)-5-$(HS)C_6H_4COOH$, 15139-21-6.

(15) For a related application of the same principle, see: Ponsati, B.; Giralt, E.; Andreu, D. *Anal. Biochem.* **1989**, *181*, 389-395.

Platina(IV) Cyclobutane Chemistry: On the Mechanism of the Ring Homologation Reaction

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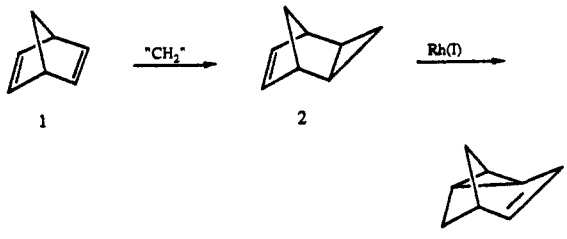
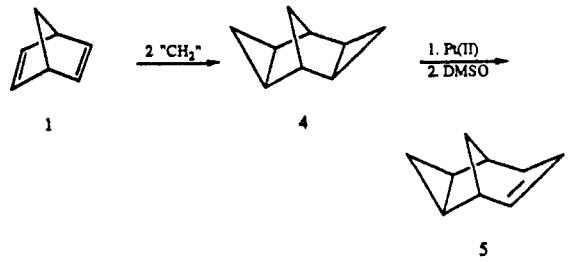
Ring or chain homologation of olefinic compounds by direct transformations using the methodology of cyclopropanation and subsequent ring cleavage has not been generally successful.[1] Thus, with the reactions shown in eq 1[2] and 2,[3] there appears to be an opportunity to facilitate this transformation. We wish to report the results of mechanistic studies involving ^2H, ^{13}C, and substitution labeling experiments with these two reactions using *platinum* as the transformation catalyst.



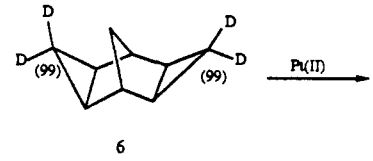
(1)

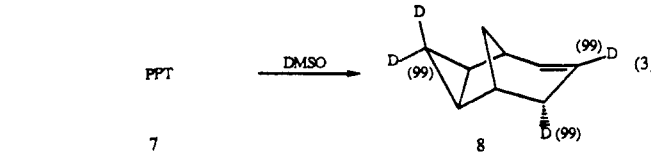


(2)

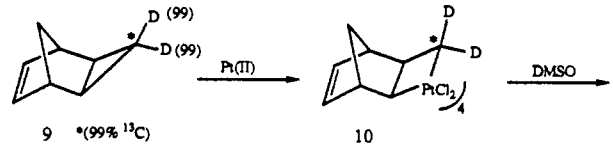
Treatment of **2** or **4** with Zeise's dimer $(C_2H_4PtCl_2)_2$ produces a light yellow solid tetrameric complex[4,5] having the platina(IV)cyclobutane moiety as shown for **10**.[6] Reaction of these metallacyclic *precipitates* from **2** and **4** with DMSO gave excellent yields of **3** (75%) and **5** (90%), respectively.[7]

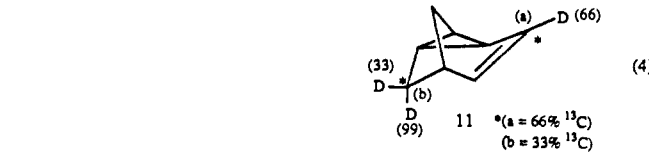
Results of the transformation with labeled substrates[8] are shown in eqs 3, 4, and 5. Numbers in parentheses represent the percent label observed by ^1H, ^2H, and/or ^{13}C NMR spectroscopy. A mechanism for reaction 3 which adequately accounts for the observed distribution of ^2H and ^{13}C in the product is shown in Scheme I.



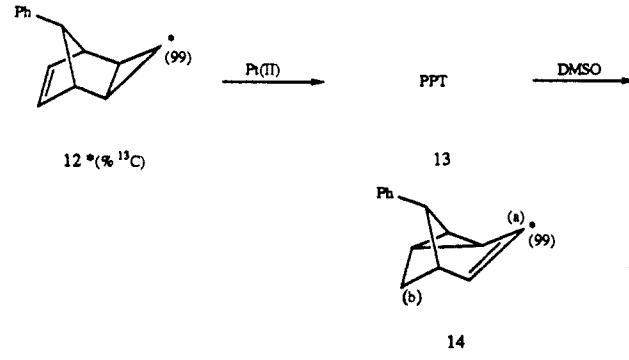


(3)





(4)



(5)

For reaction 4, a sequence proposed earlier by Katz[2] using Rh(I) would predict 99% deuterium and 100% ^{13}C at carbon (a) and 99% deuterium only in the endo configuration at carbon (b) for product **11**. This was not observed, eq 4. Thus, the three reaction pathways shown in Scheme II were considered to explain the labeling results. Path A, **16**-**18**, represents 66% of the reaction course following a path analogous to that observed by Katz with rhodium.[2] Pathway B results from bridge migration and subsequent steps. Pathway C branches from path A at intermediate **16** leading to the same product as from path B.[11] Either path B and/or C could place 33% ^{13}C at carbon b (eq 4) and 33% ^2H

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(7) In this reaction, we have recently found that higher yields are obtained when the DMSO reaction is given more time to react. It is slow at room temperature with $\kappa = 2.6 \times 10^{-4}$ s^{-1} with a $t_{1/2} = 44$ min. Thus, complete reaction of 3.4×10^{-4} moles of platinacycle required about 5 h.
(8) Compounds **2** and **4** were prepared with and without deuterium at the cyclopropyl apex methylene by use of diiodomethane (99.4% d_2) and the Simmons-Smith reagent. Further, compounds **2** and **4** were prepared with ^{13}C at the apical carbon by using diazomethane (99%^{13}C) and $Pd(OAc)_2$. All compounds were purified by preparative gas chromatography and analyzed by GC-MS and NMR spectroscopy. The proton and carbon assignments for these compounds have been thoroughly analyzed assuring adequate interpretation.[6,9,10]
(9) Campbell, W. H.; Jennings, P. W. *Organometallics* **1982**, *1*, 1071.
(10) Campbell, W. H.; Jennings, P. W. *Organometallics* **1983**, *2*, 1460.
(11) The authors are indebted to an astute referee for pointing out the possibility of path C.

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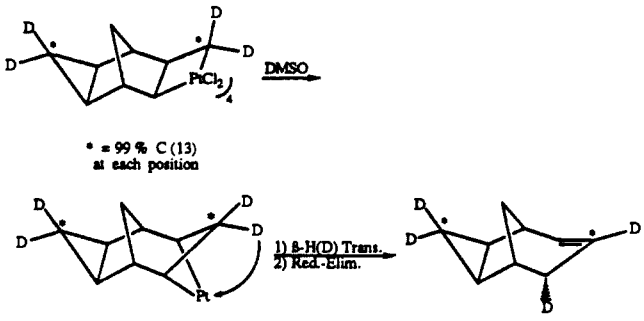
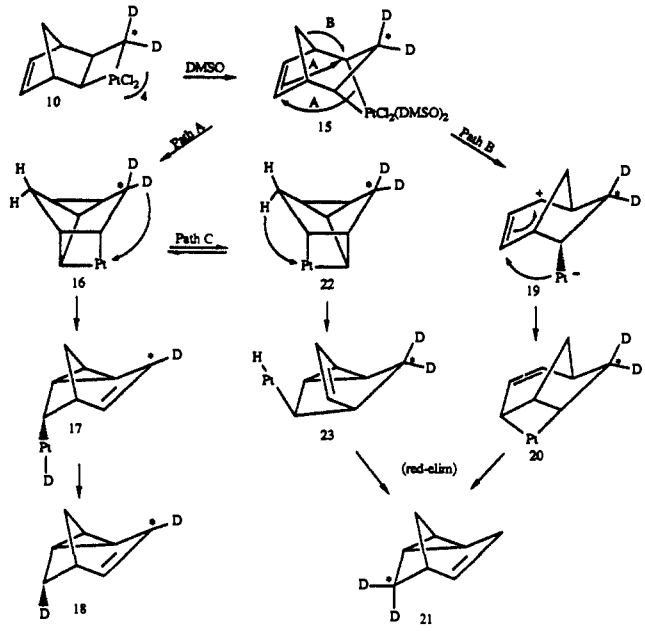
Scheme I



Scheme II



at the exo position of carbon b (eq 4). To distinguish between these two pathways, compound **12** was prepared.[12,13] Path B would *not* be adversely affected by this substitution, and path C would be *entirely precluded* since the β-hydrogen elimination is blocked by the phenyl substituent. The results are shown as eq 5. *Both pathways* (B and C) would have given ^{13}C label at carbon (b) (compare eq 5 to paths B and C in **21** Scheme II). Since the only label observed was at carbon (a), it must be concluded that path C was blocked by the phenyl substituent in **12** and B is not followed at all. Hence, it appears that path A is responsible for 66% of the product and C is responsible for 33% of the product in the Pt(II)-catalyzed transformation of **2** via the *platina(IV)-cyclobutane intermediate* which is shown as structure **10**.

Acknowledgment. Support from the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation, and Johnson-Matthey is gratefully acknowledged.

Supplementary Material Available: Spectroscopic data for **3**, **5**, **8**, **11**(D), **11**(^{13}C), and **14** (4 pages). Ordering information is given on any current masthead page.

(12) Prepared with diazomethane (99% ^{13}C), $Pd(OAc)_2$, and 7-phenylnorbornadiene (Frinton).

(13) Dissolution of **13** in pyridine and $CDCl_3$ gave the stable platina(IV)cyclobutane monomer: ^{13}C NMR ($CDCl_3$) -2.5 (t, $J_{Pt,C}$ = 375 Hz), 10.7 (d, $J_{Pt,C}$ = 406 Hz), 41.7 (d), 41.9 (d, $J_{Pt,C}$ = 22 Hz), 52.1 (d, $J_{Pt,C}$ = 84 Hz), 56.8 (d), 131.0 (d, $J_{Pt,C}$ = 28 Hz), 132.8 (d) (142.4, 128.8, 127.3, 124.8; phenyl carbons).

Electrospray Ionization: A New Tool for the Analysis of Ionic Transition-Metal Complexes

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Ionic transition-metal complexes have been difficult to analyze by mass spectrometry because of their low volatility, high thermal lability, and their tendency to undergo reduction during the ionization process.[1-6] We have succeeded in generating, by electrospray ionization, intense beams of intact gas-phase cations from ionic transition-metal complexes, such as $[Ru^{II}(bpy)_3]Cl_2$ (where bpy = 2,2′-bipyridyl) (I) and $[Ru^{II}(phen)_3]Cl_2$ (where phen = 1,10-phenanthroline) (II). In contrast to infrared laser desorption multiphoton ionization,[2] fast atom bombardment,[3,6] and field desorption,[6] the cations observed from these complexes with electrospray ionization do not undergo reduction by electron or hydrogen transfer.

Electrospray ionization is a gentle ionization technique that can produce multiply charged ions from organic molecules in solution. Several workers[7-9] have interfaced atmospheric pressure electrospray ionization sources to quadrupole mass analyzers and have obtained mass spectra from a variety of compounds including dyes, polymers, peptides, and proteins. Recently, we have designed a novel electrospray ionization source for use with a single quadrupole mass analyzer.[10] In this source, the charged droplets, produced by electrospray at atmospheric pressure, are focused and transported through a 203-mm-long stainless steel capillary tube into a region maintained at a pressure of 1-10 Torr. Controlled heating of the capillary tube assists in the evaporation of solvent from these droplets and in the desolvation of solvated analyte ions. Because complete desolvation of the analyte ions is not always achieved by heat alone, the ions exiting the capillary tube may remain partially solvated. Application of an electrostatic field in the low-pressure region between the capillary exit and a coaxial skimmer causes collisional activation of these solvated analyte ions.[10,11] This electrostatic field can be easily varied and provides a fine control over the amount of collisional activation. At low levels of activation, complete desolvation of the cations can be effected without causing fragmentation. At higher levels of activation, the desolvated cations can be induced to undergo dissociation to give structurally informative fragment ions.

The potential of the technique is evident from the electrospray ionization mass spectra (Figure 1) of $[Ru^{II}(bpy)_3]Cl_2$ (M_r = 641), obtained by electrospraying a 15 pmol/μL solution in acetonitrile. When the level of collisional activation is low (Figure 1a), the most intense peak in the spectrum corresponds to the $Ru(bpy)_3^{2+}$ ion at m/z 285.[12] The spectrum also exhibits a series of lower

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