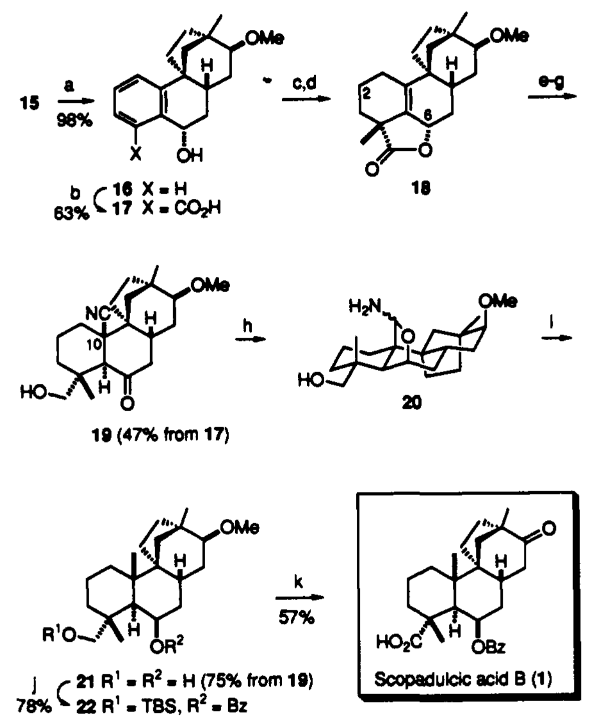
**Scheme II**[a]



[a] Reaction conditions: (a) $LiAlH_4$, THF, −78 °C; (b) *n*-BuLi (4 equiv), TMEDA–pentane, reflux; $CO_2$, 0 °C, 63% of **17** and 10% of the lactone, (c) Li, $NH_3$–THF (4:1), reflux; isoprene; MeI; (d) $H_2$, $Rh/Al_2O_3$; (e) $LiAlH_4$, THF, 0 °C; (f) $MnO_2$, $CH_2Cl_2$, 23 °C, 55% from **17**; (g) $Et_2AlCN$, PhMe, 23 °C, 85%; (h) $LiAlH_4$, THF, 75 °C; (i) $NH_2NH_2{\cdot}2HCl$, $NH_2NH_2{\cdot}H_2O$, $HOCH_2CH_2OH$, 195 °C; KOH, 195 °C, 74% from **19**; (j) TBSOTf, 2,6-lutidine, −70 °C; BzOTf, 2,6-lutidine, 23 °C; (k) TBAF, THF, 23 °C; $RuCl_3{\cdot}H_2O$, $NaIO_4$, $CH_3CN$–$CCl_4$–$H_2O$.

Reduction of this enone from the β face was best achieved by delivery of hydride intramolecularly from the C(13) alcohol.[20] This latter functionality was finally protected as a methyl ether to provide **15** in 37% overall yield from dienone **13** and set the stage for the critical functionalization of the aromatic ring.

Reduction of the α-tetralone **15** with $LiAlH_4$ at −78 °C provided the equatorial alcohol **16** in near quantitative yield. Ortho lithiation of this intermediate with excess *n*-BuLi in refluxing pentane–TMEDA[21] followed by quenching with $CO_2$ afforded the benzoic acid **17** in 53% yield together with 10% of the corresponding lactone, a byproduct that was readily converted to **17**, and 30% of recovered **16**. Birch reduction and methylation[22] proceeded to deliver, after selective saturation of the 2,3-double bond, the lactone **18** in 65% overall yield from **17**.

Completion of the synthesis of scopadulcic acid B required development of the remaining quaternary center at C(10). All attempts to directly introduce this angular methyl group by conjugate addition of methyl organometallics to various intermediates having C(6) enone functionality were unsuccessful. This last obstacle was finally surmounted in an efficient, albeit classical, fashion. Sequential treatment of **18** with $LiAlH_4$, $MnO_2$, and $Et_2AlCN$[23] provided ketone **19** in 47% overall yield from **17**. The conversion of this intermediate to alcohol **21** was greatly simplified when we discovered that reduction of **19** in THF with an excess of $LiAlH_4$ proceeded cleanly and stereoselectively to give pentacycle **20** in essentially quantitative yield. Reduction of this remarkably stable cyclic aminal could be accomplished in 74% yield, under forcing Wolff–Kishner conditions, to afford the tetracyclic diol **21**. Silylation of the primary alcohol of **21** followed by acylation of the secondary alcohol with benzoyl triflate[24] provided **22**, which was desilylated, and the resulting alcohol was oxidized with $RuO_4$[25] to afford (±)-scopadulcic acid B (**1**) in 55% overall yield from **21**. Synthetic **1** showed 500-MHz $^1H$ NMR, 125-MHz $^{13}C$ NMR, and chromatographic properties that were indistiguishable from those of an authentic sample of **1**.

The synthesis of scopadulcic acid B (**1**) summarized in Schemes I and II is capable of providing 10–100-mg amounts of **1** and congeners for pharmacological investigation. Besides being the first successful entry to this new class of biologically active terpenoids, the efficient conversion of **10** to tetracycles **11** and **12** provides the best illustration to date of the power of intramolecular Heck cyclizations to solve formidable problems in complex molecule synthesis.

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# Ring Contraction of Cyclooctene, 1,3-Cyclooctadiene, 1,5-Cyclooctadiene, and Cyclooctatetraene to Benzene on Platinum(111) Surfaces

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We wish to report the discovery and mechanistic studies of the conversion of cyclic $C_8$ alkenes, including cyclooctene (COE), 1,3-cyclooctadiene (1,3-COD), 1,5-cyclooctadiene (1,5-COD), and cyclooctatetraene (COT), to benzene on Pt(111) surfaces under ultra-high-vacuum (UHV) conditions. This work has relevance not only for understanding important processes that occur on Pt surfaces during hydrocarbon reforming[1] but also for modeling reactions that certain organoplatinum compounds undergo during chemical vapor deposition (CVD).[2] Although the conversion of cyclic $C_6H_{6+2n}$ hydrocarbons into benzene on a Pt(111) surface is a well-known process,[3-5] the corresponding chemistry of cyclic

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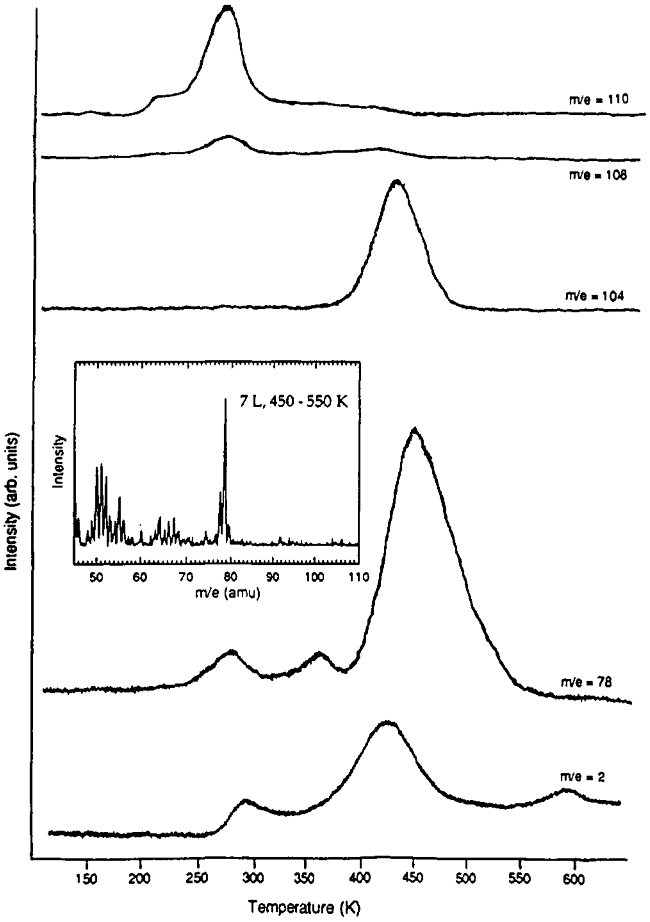

**Figure 1.** Temperature programmed desorption traces for a 7-langmuir dose of cyclooctene on Pt(111). The $m/e = 2$ channel tracks $H_2$ desorption, while the $m/e = 78$ channel contains desorption features for COE, 1,3-COD, COT, and benzene, $m/e = 104$ tracks desorption of COT, $m/e = 108$ tracks COE and 1,3-COD, and $m/e = 110$ tracks cyclooctane and COE. Inset: integrated desorption mass spectrum.

$C_8H_{8+2n}$ hydrocarbons has barely been explored. Muetterties and co-workers reported that under UHV conditions COE and 1,5-COD dehydrogenate on transition-metal surfaces (including Pt) ultimately to give COT, which can be displaced from the surface by addition of trimethylphosphine.[6,7] The subsequent fate of the adsorbed COT ring was not determined, however, and no mechanistic or spectroscopic studies of these transformations were carried out.

In our studies, the reactions of $C_8$ alkenes adsorbed on a clean (111) face of a Pt single crystal were followed by temperature programmed desorption (TPD) and integrated desorption mass spectrometric (IDMS) techniques.[8,9] In agreement with earlier work,[6,7] cyclooctatetraene does *not* desorb in significant quantities upon the heating of a Pt(111) single crystal dosed at ~120 K with low coverages (<0.5 saturation monolayers) of COT. Somewhat surprisingly, however, we find that *benzene* is the predominant gas-phase product. It desorbs in two steps with TPD peak maxima at 470 and 495 K as followed in the $m/e = 78$ channel.[10] For the other cyclic $C_8$ alkenes we have studied, heating the dosed crystal promotes several desorption/decomposition processes; in all cases, however, benzene is a significant product (Figure 1).[11,12]

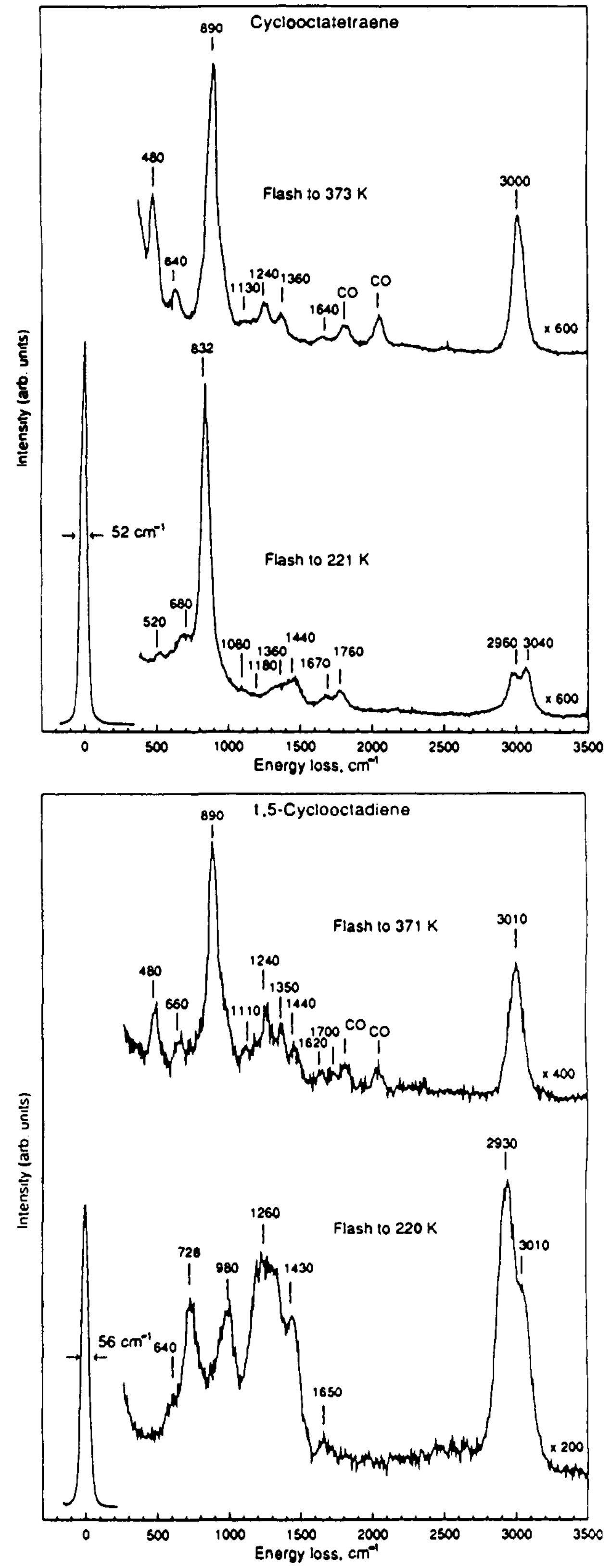

**Figure 2.** High-resolution electron energy loss spectra for 1,5-COD and COT adsorbed on Pt(111) and heated to the temperatures indicated. All HREEL spectra were recorded at 100 K.

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(8) Samples were exposed to adsorbates in two ways. Studies carried out on polycrystalline Pt foils used an effusive molecular beam doser with a 100-$\mu$m aperature. Pt single crystals were dosed from the background. Coverages are expressed as langmuirs (1 langmuir = $10^{-6}$ torr s).

(9) The structures of the desorbing products were determined by comparing the mass spectra recorded by IDMS with that from an authentic sample. Dubois, L. H. *Rev. Sci. Instrum.* **1989**, *60*, 410–413.

(10) In our system, benzene desorbs from Pt(111) at 475 K.

In contrast, cyclooctane desorbs molecularly from Pt(111) and does not undergo dehydrogenation or ring contraction. All of the $C_8$ alkenes except COT give multiple low-temperature $H_2$ desorption peaks and one high-temperature $H_2$ desorption peak near 620 K. Auger electron spectroscopy indicates that heating a saturation coverage of any of the $C_8$ alkenes to 800 K leaves about 15% of a monolayer of carbon, or about $^1/_4$ of the amount of carbon generated by heating a saturation coverage of ethylene on Pt(111).[13,14]

The similar temperatures at which benzene is formed from the different $C_8$ alkenes suggest that these reactions proceed via a common intermediate. One possibility is that the first step in the conversion of cyclic $C_8H_{8+2n}$ alkenes to benzene is dehydrogenation to COT. Support for this suggestion has been obtained from high-resolution electron energy loss spectra (HREELS) of 1,5-COD and COT on Pt(111): at 220 K (which is above the multilayer desorption temperature), both molecules retain their tub-shaped structures and are bound to the surface in an $\eta^4$ fashion (Figure 2).[15-20] By 370 K, however, both 1,5-COD and COT react to form the *same* species on the surface. In the $\nu_{CH}$ region, only one peak, at $\sim$3005 cm$^{-1}$, is observed in the HREEL spectrum. This band and those at 890 and 480 cm$^{-1}$ are consistent with the presence on the surface of a planar, dianionic $\eta^8$-COT ring.[16,21,22]

Upon further heating, the most significant reaction channel is decomposition of the $\eta^8$-COT molecules to benzene and acetylene. Subsequently, the acetylene rapidly converts to surface acetylide ($-C\equiv CH$), as shown by the presence of peaks at 3090 ($\nu_{CH}$) and 832 cm$^{-1}$ ($\beta_{CH}$) in the HREEL spectra of a surface which was flashed to 560 K.[23] At least two mechanisms could account for the formation of benzene and acetylene from the $\eta^8$-COT intermediate: (1) rearrrangement to bicyclo[4.2.0]octa-1,3,5-triene[24] followed by a [2 + 2] cycloreversion reaction to give acetylene and benzene or (2) complete decyclization of COT to four acetylene molecules, some of which then cyclotrimerize to benzene.[25] We have distinguished these possibilities by carrying out a crossover experiment. A mixture of COT and COT-$d_8$ was coadsorbed onto a Pt(111) surface, and the benzene that desorbed between 400 and 530 K was analyzed by IDMS. No benzene-$d_2$ or benzene-$d_4$ was found to be present; instead, the desorbed benzene consisted almost exclusively of the -$d_0$ and -$d_6$ isotopomers.[26] The lack of crossover rules out the complete decyclization mechanism but is consistent with the rearrangement/cycloreversion pathway.

Further studies of the reactions of cyclic and bicyclic hydrocarbons on Pt(111) surfaces are underway.

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(11) For example, 1,5-COD and 1,3-COD both give two desorption features: the first, at 405 K, consists of COT, while the second, at 445 K, consists of benzene. In contrast, cyclooctene on Pt(111) gives three separate TPD features: the desorbing flux consists of a mixture of COE and 1,3-COD between 325 and 380 K, a mixture of COT and benzene between 380 and 450 K, and benzene exclusively above 450 K. On a polycrystalline Pt foil, COT and 1,5-COD give a benzene TPD peak at 455 K.

(12) For mass spectra of all of the $C_6$ and $C_8$ hydrocarbons, see: *Atlas of Mass Spectral Data*; Stenhagen, E., Abrahamsson, S., McLafferty, F. W., Eds.; Interscience: New York, 1969; Vol. 1. No $C_2$ or $C_4$ decomposition products were detected for any of the compounds studied.

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(26) Some benzene-$d_5$ was formed that resulted from COT-$d_7$ impurities present in the sample of COT-$d_8$.

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# Ligand-Stabilized Giant Palladium Clusters: Promising Candidates in Heterogeneous Catalysis

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Large transition-metal clusters and colloids deserve notice for different reasons. They may serve as objects for the study of quantum size effects and the formation of metallic states,[1] and they are ideal candidates for catalytic processes.[2] Established methods for the preparation of large metal clusters and colloids on various supports[3-6] lead to a more or less broad size distribution.

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