Chloropalladation of Cyclopropane in Bicyclo[5.1.0]oct-3-ene and Subsequent 1,4,5-η-Cyclooctenyl to 1-3-η-Cyclooctenyl Rearrangement[1]

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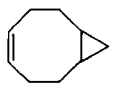
Abstract: Reaction of *cis*-bicyclo[5.1.0]oct-3(*Z*)-ene (**5**) with dichlorobis(benzonitrile)palladium(II) results in chloropalladation of the cyclopropane moiety to produce the stable di-μ-chloro-(1,4,5-η-7-chlorocyclooctenyl)dipalladium(II) (**6**). Detailed analysis of the ^{1}H NMR of **6** and a deuterated analog (prepared from *endo*-8-deuterio-**5**) leads to the conclusion that the chloropalladation is trans. The present results support the earlier proposal of cyclopropane chloropalladation in bicyclo[6.1.0]non-4-ene. However, complex **6** rearranges not to a cyclooctadiene complex, as would have been expected from the earlier work, but to the π-allylic complex di-μ-chloro-(1-3-η-5-chlorocyclooctenyl)dipalladium(II) (**13**). The bridge-cleaved pyridine derivative of **6** rearranges similarly to a π-allyl; however, the corresponding acetylacetonate derivative of **6** is stable as the 1,4,5-η-cyclooctenyl chelate and does not rearrange. Reactions of the various complexes with sodium borohydride, carbon monoxide-methoxide, and cyanide ion are described. The 1,4,5-η-cyclooctenyl to 1-3-η-cyclooctenyl rearrangement reported here has no precedent in palladium chemistry, although many palladium 1,4,5-η-cyclooctenyls are known. The unusual hydrogen lability in **6** and its pyridine derivative is not well understood.

Addition of Pd-Cl to carbon-carbon bonds is an important general organopalladium reaction.[2] Use of the cyclopropane ring as a substrate in this reaction has been limited to vinylic cyclopropanes,[3] to dicyclopropanes,[4] and to bicyclo[6.1.0]non-4-ene.[5] In the vinylcyclopropane additions, there is no direct evidence for initial Pd(II) or Pd-Cl attack at the cyclopropane moiety; however, it has been suggested that olefin coordination in the vinylcyclopropanes facilitates ring opening via a cyclopropylcarbinyl-homoallyl rearrangement.[3a] We reported earlier[5] on the addition of Pd-Cl to the "nonconjugated" cyclopropane in bicyclo[6.1.0]non-4-ene (**1**) leading finally to dichloro(1,2:5,6-η-*cis*,*cis*-cyclononadiene)palladium(II) (**2**). The initial olefinic coordination of **1** to Pd(II) was followed first by chloropalladation to give complex **3** and then by dechloropalladation and hydrogen migration to give **2.** It was also found[5] that dichlorobis-



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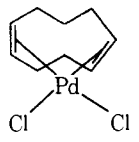

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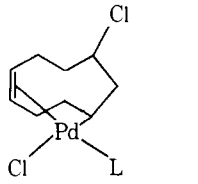
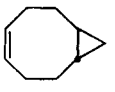
(benzonitrile)palladium(II) catalytically converts **1** to *cis*,*cis*-1,5-cyclononadiene, and that the chloropalladation complex, **3**, reacts with aqueous cyanide to liberate *trans*-bicyclo[6.1.0]non-4-ene (**4**).



L = half-dimer or PhCN

3



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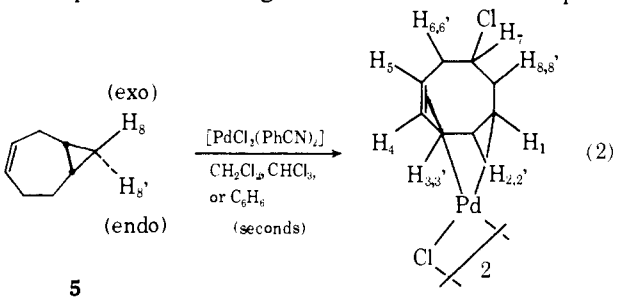
To continue our study of organometallic reactions of cyclopropane rings which are remote from double bonds and which are not subject to significant additional ring strain, we report here on the reaction of bicyclo[5.1.0]oct-3-ene with dichlorobis(benzonitrile)palladium(II). This reaction involves trans Pd-Cl addition to cyclopropane. However, in contrast to the previous work, there is no subsequent formation of *cis*,*cis*-1,5-cyclooctadiene, nor have we detected any *trans*-bicyclo[5.1.0]oct-3-ene. Also in contrast to the work with bicyclo[6.1.0]non-4-ene, the initially formed 1,4,5-η-7-chlorocyclooctenyl complexes reported here rearrange readily to 1-3-η-5-chlorocyclooctenyl derivatives (π-allyls).

Results

Bicyclo[5.1.0]oct-3-ene (**5**) reacts in seconds at room temperature with $[PdCl_2(PhCN)_2]$ to give the chloropalladation product **6.** During the reaction at room tempera-



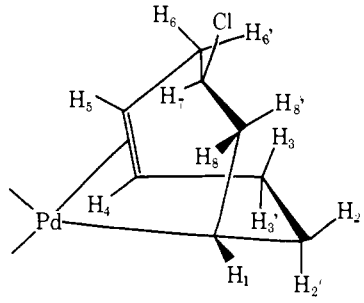
(2)

5

6

ture no preliminary formation of a π-olefin complex (with the cyclopropane intact) could be demonstrated using NMR or ir techniques. However, olefin coordination prior to cyclopropane ring opening was detected at −20° in $CDCl_3$. Thus, chilled $CDCl_3$ solutions, one 0.06 *M* in $[PdCl_2PhCN_2]$ and the other 0.06 *M* in **5**, were mixed at −20°, and the ^{1}H NMR spectrum was recorded at once. The spectrum obtained showed a resonance for coordinated olefin at δ 6.3 (2 H), with little change elsewhere on comparison with the spectrum of **5** in $CDCl_3$ at −20°. In particular the cyclopropane resonances were virtually unchanged, while the olefinic resonance shifted to low field by 0.7 ppm on coordination.[5] Little change was observed in the spectrum over 45 min at −20°; however, after 45 min the solution was warmed to room temperature for 2 min after which only the ^{1}H NMR spectrum of **6** was observed. Complex **6** is stable and is easily isolated. The ir spectrum of **6** has bands characteristic[6] of coordinated olefin (1465 cm^{-1}),

C-Cl stretching (750 cm^{-1}), and bridging chlorine (286 (s), 224 (s), 210 (s, sh) (cm^{-1})). The most likely conformation of the cyclooctenyl ligand in **6** has been deduced from the ^1H NMR spectra, obtained at 60, 100, and 220 MHz. This chair-like conformation is shown below as **7** (chair). The coordinated ligand in **7** results from trans chloropalladation with the added chlorine taking an equatorial position in the coordinated cyclooctenyl ring. Conformation **7**



7 (chair)

also is believed present in the bridge-cleaved derivatives of **6**, since the ^1H NMR's are similar. The ^1H NMR spectrum of **6** at 100 MHz is described as follows (see Figure 1): at low field there is a pair of 1-H four line multiplets (H_4 and H_5, δ 6.35, $J_a = J_b = J_{4,5} = 7.4$ Hz; and δ 5.68, $J_{4,5} = 7.4$ Hz, $J_c = J_d = 8.2$ Hz). A nearly symmetric 1-H 12-line multiplet is found at δ 4.56 (H_7, $J_e = J_f = 12.4$ Hz; $J_g = 4.8$ Hz, $J_h = 3.8$ Hz). A 1-H multiplet (H_1) occurs at δ 3.9-3.5. There is a series of multiplets from δ 2.8 to 1.6 (6 H, assignments uncertain), and a 2 H multiplet at δ 1.2-0.7. At 220 MHz it is apparent that this last multiplet is a composite peak made up of (a) a double doublet (δ 0.97, $J_i = 14.5$ Hz, $J_j = 7.0$ Hz) and (b) a triple doublet (δ 0.88, $J_k = 12.4$ Hz, $J_l = 12.4$ Hz, $J_m = 3.5$ Hz). The H_1, H_4, and H_5 assignments are consistent with earlier results for model halogen-bridged 1,4,5-η-cyclooctenyl complexes of palladium[7a,b] and nickel,[7c,d] and the resonance for H_7 lies in the expected range for hydrogen α to chlorine.[8] In addition, in support of the H_1 assignment, it was found that the resonance assigned to H_1 moves nearly 0.5 ppm to higher field in the acetylacetonate derivative of **6** (complex **12**, below), while the other resonances, particularly that assigned to H_7 in **12**, are little changed.

It was found by double irradiation at 100 and 220 MHz that both H_1 and H_7 are coupled to the hydrogen giving rise to the highest field triple doublet at δ 0.88. We infer that this triple doublet arises from one hydrogen which lies between H_1 and H_7—either H_8 or $H_{8'}$. Therefore $J_{7,8}$ *or* $J_{7,8'} = 12.4$ Hz and $J_{1,8}$ *or* $J_{1,8'} = 3.5$ Hz.

The ^{13}C NMR spectrum of **6** shows the expected eight resonances for the cyclooctenyl ligand. Recording of the spectrum using off-resonance decoupling conditions showed that four of the carbons have only one hydrogen, while the remaining four have two, as expected. The results are as follows (δ, ppm referenced to TMS): 112.2 and 97.98 (coordinated olefinic carbons); 59.34 and 54.00 (Pd-C-H and >CHCl); 45.81, 42.53, 35.80, and 23.84 (remaining CH_2's).

The substitution pattern in **6** is established as follows: since both H_4 and H_5 are nearly equally coupled to *three* other vicinal hydrogens, the fragment $-(CH_2)CH{=}CH(CH_2)-$ is present. H_7 is coupled vicinally to *four* hydrogens, implying the presence of the $-CH_2CHClCH_2-$ fragment. Both H_1 and H_7 are vicinally coupled to H_8 or $H_{8'}$, implying the $-CClHCH_2CH(Pd)-$ fragment. Finally, degradation studies (below) of **6** have proved that the $=CH(CH_2)CClH-$ unit is present. Therefore, **6** is a 1,4,5-η-cyclooctenyl resulting from Pd-Cl addition to the internal cyclopropane C-C σ bond in **5.** The trans stereochemistry of Pd-Cl addition is discussed below.

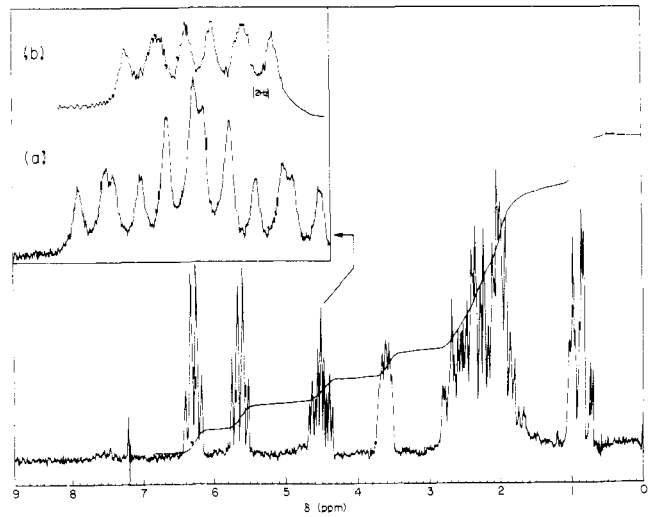
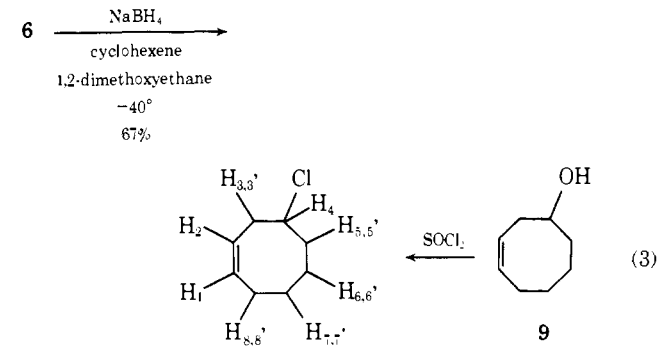
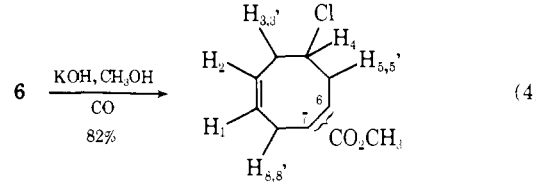


Figure 1. ^1H NMR spectrum of di-μ-chloro-bis(1,4,5-η-7-chlorocyclooctenyl)dipalladium(II) (**6**) in $CDCl_3$ at 100 MHz. Inset: (a) expansion of the δ 4.56 multiplet (100 MHz); (b) expansion of the δ 4.56 multiplet in **6**(endo-D) (see text) (60 MHz).

Complex **6** reacts with sodium borohydride under conditions[9] which minimize rearrangement and/or olefin reduction, yielding 4-chlorocyclooctene, **8.** Chlorination of **9**[10] also gave **8**, which, together with double irradiation experiments (experimental section), established the structure of **8.**



Reaction of **6** with carbon monoxide in basic methanol[11] gave the methyl ester **10.** The available ^1H NMR data unfortunately do not distinguish positions 6 or 7 as the site of $-CO_2CH_3$ attachment in **10**; however, there is every reason to expect that C_6 is the site of attachment.[12]



Treatment of **6** with aqueous cyanide liberates only the starting bicyclo[5.1.0]oct-3-ene, **6** (92%).

The chlorine bridge in **6** is cleaved both by pyridine (py) and by sodium acetylacetonate to give derivatives **11** and **12.**[13] Complexes **6** and **11** were found to rearrange to the

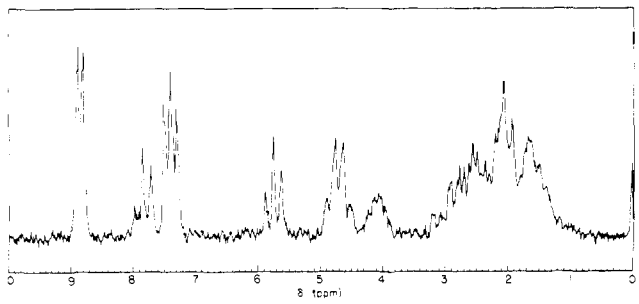
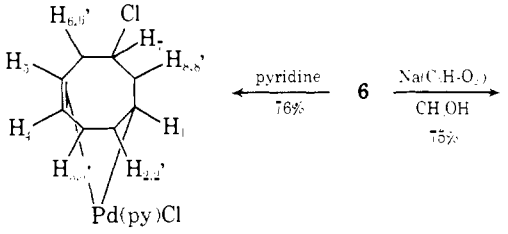


Figure 2. ^{1}H NMR spectrum of chloropyridine(1-3-η-5-chlorocyclooctenyl)palladium(II) (**14**) in $CDCl_3$ at 60 MHz.



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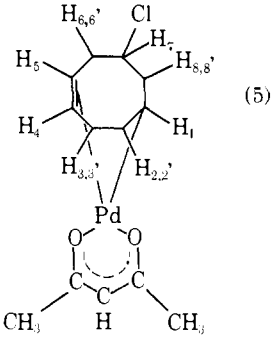

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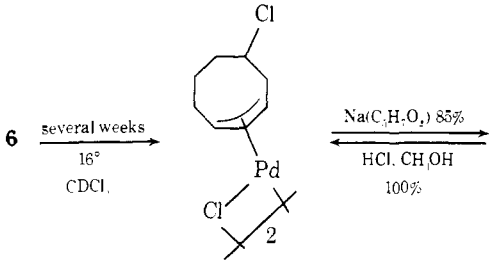
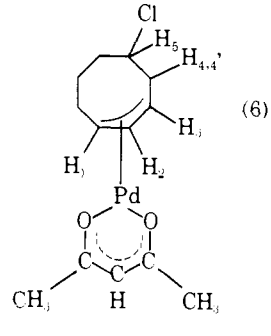
isomeric 1-3-η-cyclooctenyls, **13** and **14**. Solutions of **6** (0.04–0.11 *M*) in $CDCl_3$ were found to rearrange to **13**



13



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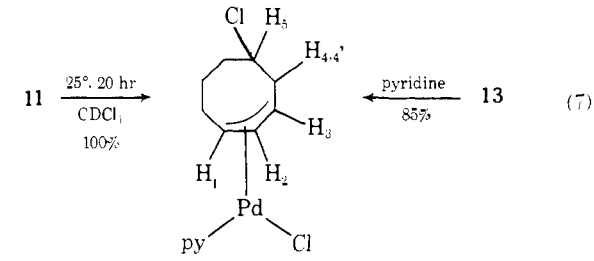
with half-lives of several weeks at 16° (in the dark). The reaction rate was not significantly dependent upon concentration in this range, but was accelerated several-fold by

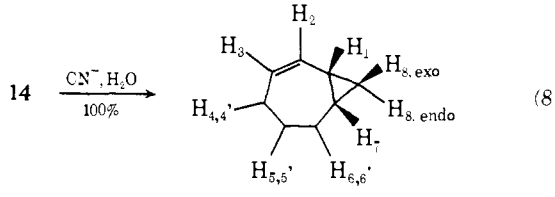


14

small amounts of benzonitrile. At 55°, a 0.11 *M* solution of **6** in $CDCl_3$ (PhCN free) rearranged to **13** with a half-life of about 4 hr. The pyridine derivative **11** rearranges to the allylic isomer **14** much faster than in the **6** → **13** reaction. Thus a half-life of about 4 hr was observed for a 0.12 *M* solution of **11** in $CDCl_3$ at 25°. In contrast to **6** and **11**, **12** would not rearrange directly to isomer **15**. It was observed that **12** had undergone ~40% decomposition (to Pd^0 and other unknown product(s)) on heating a $CDCl_3$ solution to 55° in the dark for 18 hr. There was no accumulation or observation of **15** during this period. Under the same conditions, however, **15** is relatively stable, with only ~15% decomposition being observed (**15** is easily prepared from **13** (eq 6)). It was also found that complex **12** in $CDCl_3$ (0.12 *M*) fails to rearrange to an allylic isomer within 18 hr at 25°. At the end of this period there had been ~30% decomposition of **12** to palladium metal and unknown organic product(s), but allylic resonances were undetectable by ^{1}H NMR.

The 1-3-η-5-chlorocyclooctenyl complexes **14** and **15** have characteristic ^{1}H NMR spectra (see Figure 2). The central allylic hydrogen in each appears as a low field triplet at δ 5.75 (**14**) and 5.66 (**15**) with J = 7–8 Hz, due to approximately equal vicinal coupling with the two terminal allylic hydrogens. The terminal allylic hydrogens give rise to broad quartets at δ 4.70 (**14**) and 4.53 (**15**), again with J = 7–8 Hz due to approximately equal coupling with the three vicinal hydrogens. The low field triplet is especially diagnostic of the unsubstituted cyclic allyl structure.[14]

Complex **14** was reduced with sodium borohydride to give 4-chlorocyclooctene, **8**, in 50% yield. Treatment of **14** with aqueous cyanide results in 100% conversion to the known[15] bicyclo[5.1.0]oct-2-ene, **16**. Acetylacetonate **15**



(8)

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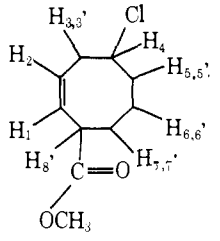
reacts with HCl to give **13** (eq 6) and with aqueous cyanide to give **16** (89%). Complex **13** also reacts with aqueous cyanide to give a quantitative yield of **16**. Reaction of both **13** and **14** with carbon monoxide in basic methanol gives a methyl ester (**17**) which is isomeric with **10**. In support of the assigned structure for **17**, we observe that irradiation of



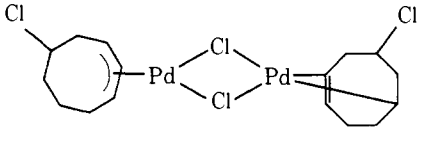
17

the H_8 multiplet narrows the olefinic pattern by 6–7 Hz, implying the vicinal arrangement of H_1 and H_8.

The major difference in the ^1H NMR's of **10** and **17** is the location of the resonance assigned to hydrogen α to $-CO_2CH_3$ (H_8 in **17** at δ 3.9–3.4; H_6 in **10** at δ 3.2–2.6). The deshielding of this resonance in **17** relative to **10** arises from the double bond adjacent to H_8 in **17.** All of the isomeric methyl esters of cyclooctenecarboxylic acid have been previously prepared[16] and examined by ^1H NMR. Methyl *cis*-2-cyclooctene-1-carboxylate has the methine resonance at δ 3.6–3.2, while methyl *cis*-4-cyclooctene-1-carboxylate has its methine resonance at higher field than δ 2.4.[16] These results support our structural assignments for **10** and **17.** Potential complications in carbonylation of allyls in basic methanol would be competititve decomposition to olefin[17] (in this case to **8**) or attack of methoxide at a terminal allylic carbon to give a methoxychlorocyclooctene. Carbonylation of both **13** and **14** gave excellent yields of **17**, however. In addition, we showed that, in the *absence* of CO, complex **14** did not react with KOH-CH_3OH (25 min at 25°) to produce detectable (by NMR) amounts of either **8** or chloromethoxycyclooctenes. Thus, on treatment of the reaction mixture with cyanide, only the expected NMR spectrum of bicyclo[5.1.0]oct-2-ene, **16**, was observed in the carbon tetrachloride extract.

The ^1H NMR spectra of **14** and **15** (and the precursor to **13**, below) definitely imply the allylic structures which are assigned. The reactions of **13–15** with cyanide to give **16**, the reduction of **14** to give **16**, the reduction of **14** to give **8**, and the reaction of **13** to give **17** all imply that the chlorine substituent is at C_5 rather than C_6 (the C_4 position is ruled out by the ^1H NMR results).

After its initial precipitation, complex **13** is virtually insoluble in common solvents. We have a number of reasons for preferring the chlorine-bridged dimeric 1-3-η-5-chlorocyclooctenyl structure shown for **13.** During the **6** → **13** rearrangement in $CDCl_3$, resonances characteristic of the 1-3-η-5-chlorocyclooctenyl ligand are observed prior to precipitation of **13.** Thus, the 220-MHz spectrum of a $CDCl_3$ solution initially 0.10 *M* in **6** shows new resonances (additional to those of remaining **6**) after 13 days (see Figure 3): a low-field triplet[18] (δ 5.54, J = 8.0 Hz), a quintet[18] (δ 4.76, J = 8.0 Hz), and a multiplet (δ 3.98, width at half-height ~26 Hz) (there are also changes in the spectrum at higher field). The relative areas of the new δ 5.54, 4.76, and 3.98 absorptions are 1:2:1, respectively, and, these are assigned to the central allylic H, terminal allylic H, and Hα to chlorine in a 1-3-η-5-chlorocyclooctenyl ligand. The substance giving rise to the new resonances is most likely to be half-rearranged **18**, because only about 25% of the 1,4,5-η



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ligands in **6** have rearranged under the conditions stated above (according to the integral ratios) and because **13** is insoluble in $CDCl_3$. We have, however, observed that **13** will dissolve in $CDCl_3$ containing excess $[PdCl_2(PhCN)_2]$. The ^1H NMR spectrum (60 MHz) of this solution has the characteristic triplet at δ 5.75 (1 H, J = 7.5 Hz), a multiplet at δ 5.03 (2 H, appears to be a triplet with J = 7.5 Hz, with weak outer lines), and a 1 H multiplet due to Hα to chlorine at δ 4.0–3.4. The species in solution is thus believed to be a cyclic allyl resulting from insertion of one or more $PdCl_2$ units into the bridge of **13.**[19] Comparison of the ^1H

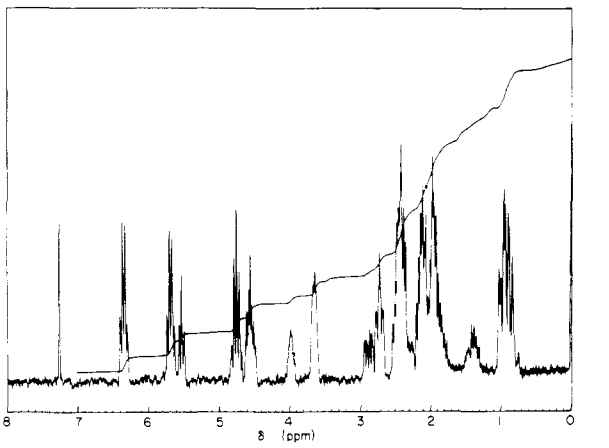


Figure 3. A 220-MHz ^1H NMR spectrum of the $CDCl_3$ solution of di-μ-chloro-bis(1,4,5-η-7-chlorocyclooctenyl)dipalladium after standing at ca. 16° for 13 days.

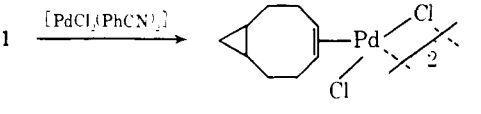
NMR of **14**, the new species **18** in the aged solution of **6**, and of **13** dissolved in the presence of $[PdCl_2(PhCN_2)]$ leaves little doubt concerning the 1-3-η-5-chlorocyclooctenyl structure for **13.** In addition the far-ir spectrum of **13** has bands at 262 (s) and 242 cm^{-1} (m), characteristic[20] of the symmetric Pd_2Cl_2 bridge. Finally, both **14** (the structure of which is reasonably certain) and **13** carbonylate to give the same ester, **17**, and both **14** and **13** react with cyanide to give olefin **16.**

In an attempt to examine the generality of the 1,4,5-η- to 1-3-η-cyclooctenyl rearrangement, we performed several experiments with di-μ-chloro-bis(1,4,5-η-8-methoxycyclooctenyl)dipalladium(II) and di-μ-chloro-bis(1,4,5-η-8-diethylmalonatocyclooctenyl)dipalladium(II). We could find no evidence for rearrangement of either of these compounds to the 1-3-η-cyclooctenyl isomers, in $CDCl_3$ at 25 or 55°, for periods up to 41 hr. Similarly, in the presence of 2 equiv of pyridine at either 25° or 55° in $CDCl_3$, there is no observed rearrangement of either complex to an allylic isomer for periods up to 41 hr. In all cases, however, palladium metal was deposited over a period of hours and unknown organic by-products were observed by ^1H NMR (10–100% decomposition was observed, depending upon conditions).

We finally observe that, under the conditions used in reactions of **5** with $[PdCl_2(PhCN)_2]$, there is no significant reaction of bicyclo[5.1.0]octane with $[PdCl_2(PhCN)_2]$.

Discussion

In the previous work with bicyclo[6.1.0]non-4-ene (**1**), we were able to isolate and characterize olefin complex **19.**[5]



(9)

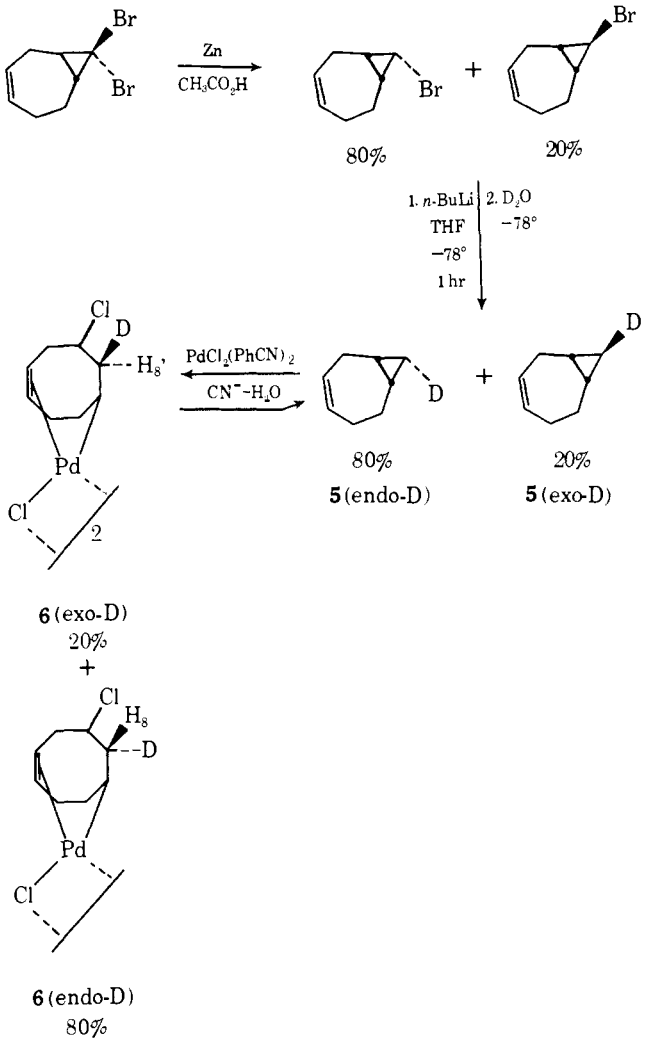
19

Complex **19** is, however, unstable toward rearrangement to **3** via chloropalladation, and **3** readily rearranges to the cyclononadiene complex **2.** Complex **3** was not isolable,[5] but we proposed the 1,4,5-η-8-chlorocyclononenyl structure on the basis of its ^1H NMR spectrum (-C*H*Cl- at δ 4.6–5.0 and -C*H*Pd- at δ 3.5–4.0), and on the basis of the remarkable reaction of **3** with cyanide ion to give *trans*-bicyclo[6.1.0]non-4-ene (**4**). In contrast to the earlier work we have only been able to detect formation of a π-olefin complex of bicyclo[5.1.0]oct-3-ene (**5**) and Pd(II) at −20°. This complex rearranges in seconds at room temperature to the relatively stable 1,4,5-η-7-chlorocyclooctenyl complex **6**

arising from trans addition of Pd-Cl to the cyclopropane. The ^{1}H NMR spectrum of **6** is in excellent agreement with the earlier assignment for **3.**

In order to conclusively interpret the ^{1}H NMR spectrum of **6** in terms of conformation **7** (chair), it was necessary to prepare the deuterated analog, **6** (endo D), from *endo*-8-deuterio-*cis*-bicyclo[5.1.0]oct-3(*Z*)-ene (**5**) (endo D), as shown in Scheme I. The ^{1}H NMR of **6** (endo-D) was obtained at 60 and 300 MHz (the small percentage of **6** (exo-D) was barely detectable). The ^{1}H NMR is similar to that of **6** with the following exceptions. (a) The 12-line multiplet at δ 4.56 in **6** (assigned to H_7) is reduced to a six-line multiplet in **6** (endo-D) (see inset B Figure 1). The six-line multiplet (with broadening of lines 2 and 5) is accounted for by $J_{6',7}$ = 12.4 Hz and two other couplings of 4.8 and 3.8 Hz ($J_{6,7}$ and $J_{7,8}$ in **7** (chair)). Thus the coupling that is lost in **6** (endo-D) is the large trans $J_{7,8'}$ = 12.4 Hz. (b) The highest field triple doublet in **6** at δ 0.88 is undetectable at 60 MHz but a weak resonance at δ (0.88) is observed at 300 MHz. This resonance is a poorly resolved double doublet ($J_{7,8'}$ = 12.4 Hz, $J_{1,8'}$ = 3.5 Hz) assigned to $H_{8'}$ in **6** (exo-D) (Scheme I). The δ 0.88 double doublet is ca. 20% of the intensity of the δ 0.97 double doublet, consistent with the 80/20 endo/exo deuteration mixture. (c) The resonance assigned to H_1 in **6** at δ 3.9-3.5 is slightly narrowed in **6** (endo-D) (by ca. 3 Hz) and at 300 MHz it appears to be an overlapping double doublet with possible additional small coupling (observed J's are 11 and 4 Hz).

Scheme I



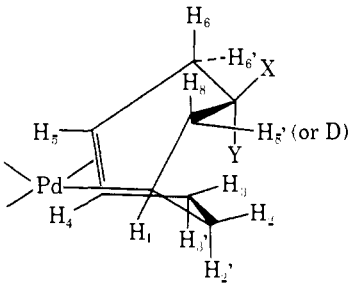
The experimental results for **6** (endo-D) are fully consistent with conformation **7**, with the assignments made for the ^{1}H NMR of **6**, and with the ^{1}H-^{1}H spin decoupling which was described above. With D in the 8′ position we now have established that $J_{7,8'}$ = 12.4 Hz and $J_{1,8'}$ = 3.5 Hz.

The chelate ring in **6** is evidently rigid. The ^{1}H NMR spectrum (60 MHz) is unchanged over the range −60 to +65°, and, in addition, the vicinal couplings are generally too large to be conformationally averaged (couplings to H_7 of 12.4 Hz, couplings to olefinic H of 7.4 to 8.2 Hz). The ^{1}H NMR results require a conformation where (a) $J_{5,6} \simeq J_{5,6'}$ and $J_{3,4} \simeq J_{3',4}$, all of these couplings being relatively large (7.4 or 8.2 Hz, in pairs), and (b) H_7 is situated at angles of ~0 or ~180° to two vicinal hydrogens (two 12.4 Hz couplings) and gauche to two others (the 3.8 and 4.8 Hz couplings). We have utilized the equations of Garbisch[21,22] to relate the H_4 and H_5 vicinal couplings to dihedral angle (φ). We find that $J_{5,6} \simeq J_{5,6'}$ for $\varphi_{5,6} \simeq 10°$ and $\varphi_{5,6'} = 130°$. Similarly $J_{3',4} \simeq J_{3,4}$ for $\varphi_{3',4} \simeq 10°$ and $\varphi_{3,4} \simeq 130°$. These dihedral angles are fully realizable in a molecular model of **7** (chair), which fulfills condition a. In **7** (chair) H_7 is forced into a trans ($\varphi \simeq 180°$) relationship with $H_{6'}$ and $H_{8'}$ and into a gauche ($\varphi \simeq 60°$) relationship with H_8 and H_6, thus fulfilling condition b (dihedral angles estimated to be ±20°). The *sizes* of the observed couplings are also reasonable for the assigned conformation. The Garbisch equations predict[21] $J \simeq 6.5$ Hz for the vinyl-allylic coupling at $\varphi \simeq 10$ or 130°, and Anet[23] observed J_{trans} = 11.4 Hz and J_{gauche} = 4.2 Hz for Hα to acetate in 3,3,4,4,5,5-hexadeuteriocyclohexylacetate.

The ^{1}H NMR results are in complete agreement with **7** (chair). Further we are able to eliminate alternate structures, as discussed in the following paragraphs.

Conformation **7** (chair) with H_7 and Cl *reversed* (which could result from overall cis addition) is ruled out by the ^{1}H NMR data due to the size of $J_{7,8'}$ (12.4 Hz). In the reversed structure $\varphi_{7,8'}$ would be close to 60°. In fact all the couplings to H_7 would be of intermediate size, and the observed pattern of two large and two intermediate couplings would not be observed.

A second conformation possibility, **7** (boat), is also ruled out by the ^{1}H NMR results. In the case of either cis Pd-Cl addition to give **7**(boat, **a**) or trans addition to give **7**(boat, **b**) the expected $\varphi_{7,8'}$ is close to 60° which could not account for $J_{7,8'}$ = 12.4 Hz.

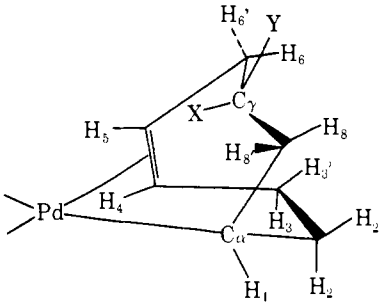


7 (boat)

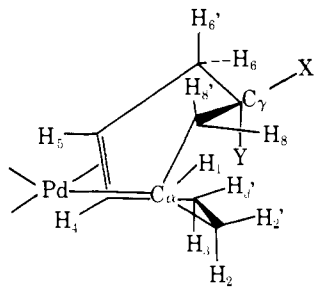
a, X = Cl; Y = H_7 (cis Pd-Cl addition)
b, X = H_7; Y = Cl (trans Pd-Cl addition)

In the preceding analysis we have assumed that palladium coordinates the olefin, **5**, on the side of the molecule trans to $H_{8'}$ to give **7**(chair). It is possible that the palladium coordinates the olefin in the opposite sense, cis to $H_{8'}$. In that case the initial coordination could be followed by overall trans Pd-Cl addition (with inversion at C_α) (case A) or overall cis addition (with inversions at *both* C_α and C_γ!)

(case B). The 1,4,5-η^3-cyclooctenyl chelate cannot be formed when palladium attacks from the side cis to $H_{8'}$ without inversion at C_α. This inversion has the effect of interchanging the roles of H_8 and $H_{8'}$ (or D in the 8′ position on **5**) on comparing **7** and either of cases A or B. The resulting structures are shown. Case A is inconsistent with the ^1H NMR results in *either* conformation because $\varphi_{7,8'}$ is ca. 60° in either case, and furthermore case A should trans-eliminate Pd-Cl on treatment with CN^-–H_2O with inversion at C_γ to give 80% **5** (exo D) and 20% **5** (endo D). In fact we recovered 80% **5** (endo D)/20% **5** (exo), unchanged overall from the starting mixture.



(chair)



(boat)

case A, X = H_7; Y = Cl (overall trans)
case B, X = Cl; Y = H_7 (overall cis)

(H_8 and $H_{8'}$ are correlated with assignments made in **5**, and D would be in the 8′ position)

Case B (chair) has $\varphi_{7,8'}$ ca. 60° and is therefore ruled out by the ^1H NMR results. Case B (boat) is consistent with the ^1H NMR results, although it is unlikely because of the implied two-carbon inversions necessary to achieve the structure. Case B (boat) may be ruled out because CN^-–H_2O induced cis elimination of Pd-Cl would give 80/20 **5** (exo-D)/**5** (endo-D) (the reverse of the experimental result), and CN^-–H_2O induced trans Pd-Cl elimination would give *trans*-bicyclo[5.1.0]oct-3(*Z*)-ene—none of which is detectable. Case B (chair) is also ruled out by the same Pd-Cl elimination arguments.

In summary, all the evidence points to initial coordination of palladium to the olefinic moiety of **5** on the side trans to $H_{8'(endo)}$. The coordination is followed by overall trans Pd-Cl addition to C_α–C_γ, with inversion at C_γ, to give the coordinated ligand in conformation **7** (chair). Reaction of **6** or **6** (endo-D) with CN^-–H_2O induces a trans Pd-Cl elimination (inversion at C_γ) to give back **5** or **5** (endo-D).

In the earlier work, we proposed cis chloropalladation of bicyclo[6.1.0]non-4-ene.[5] Cis addition was favored because the reactions were conducted in solvents of low polarity and without added chloride, both of which discourage trans addition by an ionic pathway. The present NMR data conclusively establish trans chloropalladation of bicyclo[5.1.0]oct-3-ene. The idea that trans Pd-Cl addition can be a facile process in low polarity solvents is somewhat hard to accept. However, in our own work with halopalladation of 7-methylenebicyclo[2.2.1]hept-2-enes,[6a] we have shown that trans Pd-Cl addition to the exocyclic olefin is extremely fast in the same low polarity solvents employed in the present work. Also very recently Wipke and Goeke[24] reported the trans addition of Pd-Cl to the norbornene double bond in *endo*-5-vinylbicyclo[2.2.1]hept-2-ene, using benzene as solvent. These trans additions of Pd-Cl to olefin were the first to be reported and they are believed to proceed by ionic dissociation of Pd-Cl followed by C-Cl bond formation or by bimolecular interaction of Pd-Cl with the activated ("coordinated"?) carbon-carbon bond.

In marked contrast to **3**, which gives **4** on treatment with cyanide, complex **6** reacts with aqueous cyanide to yield only the starting **5**. The absence of *trans*-bicyclo[5.1.0]oct-3-ene could be due to thermodynamic factors. Gassman and coworkers[25] have, however, prepared *trans*-bicyclo[5.1.0]oct-3-ene, which demonstrates that the molecule is not so strained that it is not approachable by conventional methods.

It is very likely that in the decomposition of **6** by cyanide a second inversion of $>C_\gamma HCl$ occurs via intramolecular displacement of $\geqslant C_\gamma$–Cl by Pd-CH< . Successive inversions would naturally regenerate starting **5**. If this view is correct, the formation of **4** would be accommodated by cis Pd-Cl addition to **1** to form **3** and Pd-Cl elimination with inversion at >CHCl to form the trans-fused cyclopropane.

The reactions of **13–16** with aqueous potassium cyanide could be viewed as a reversal of the Pd-Cl addition to a vinylcyclopropane (namely bicyclo[5.1.0]oct-2-ene, **16**). Vedejs and coworkers[3c] commented on the easy reversibility of such additions in the presence of nucleophiles. In the present case and in Vedejs' [3c] work the cyclopropane ring is regenerated and the starting vinylcyclopropane may be recovered.

In contrast, however, the allylic products resulting from chloropalladation of vinylcyclopropane in turn react with dimethyl sulfoxide to give 1,3-pentadiene.[3b] In this latter case hydrogen migration evidently competes successfully with ring closure. In the reactions of **13–15** with cyanide we observe no hydrocarbons resulting from hydrogen migration, nor do we observe any bicyclo[3.3.0]oct-2-ene, which would result from ring closure involving the terminal allylic carbon which is remote from >CHCl. These reactions are therefore remarkably selective, as is the carbonylation-ester formation reaction of **13** and **14** and the borohydride reduction of **13**, where the "remote" allylic carbon is in both cases the site of attack.

Once complex **6** is formed, it has considerable kinetic stability, in contrast to intermediate **3**. The relatively slow rearrangement of **6** to the allylic isomer **13** contrasts with (a) the rearrangement of **3** to the *cis,cis*-1,5-cyclononadiene complex **2**; (b) the absence of reports of such rearrangement in other 1,4,5-η-cyclooctenyl complexes of palladium(II);[7a,b,26] and (c) our inability to effect such rearrangement in two of the previously known systems. It is possible that point a is related to differing initial chloropalladation stereochemistries (cis for **1**?; trans for **5**), which could make Pd-Cl elimination from **6** to form cyclooctadiene an unfavorable process. Points b and c are poorly understood. All of the 1,4,5-η-cyclooctenyls of palladium(II) known previously have been prepared by nucleophilic attack on dihalo(*cis,cis*-1,5-cyclooctadiene)palladium(II) species,[7a,b,26] and all therefore have a substituent (residue of the attacking nucleophile) in the 8-position, believed to be situated trans to the Pd-C σ bond.[27] Complex **6** and derivatives have γ-substituents, and this evidently either enhances reactivity or makes the allylic isomer the more stable (the 1,4,5-η^3 isomer could conceivably be the more stable in the trans β sub-

stituted systems). The rearrangements of **6** and **11** to allylic isomers are most likely to proceed by allylic hydrogen abstraction[28] or by successive β-hydrogen eliminations.[29] In either case a vacant or easily vacated coordination site should facilitate the hydrogen transfer. Bridge cleavage in **6**[30] or pyridine dissociated in **11** could lead to a binding site for hydrogen, but in **12** the chelated acetylacetonate is not likely to dissociate and therefore no rearrangement to the allylic isomer is observed. The absence of other examples of 1,4,5-η-cyclooctenyl to 1-3-η-cyclooctenyl rearrangements in palladium(II) complexes is perplexing in view of our results, since there is no obvious reason for lack of hydrogen migration in the previously known complexes. It is possible that the differing reactivities of the two types of 1,4,5-η-cyclooctenyls can be attributed to differing conformations of the coordinated eight-membered rings, or to unusual lability of the carbon–chlorine bond.

Experimental Section

Microanalysis for C, H, and Cl was performed by C. F. Geiger, Ontario, Calif., and by Chemalytics, Inc., Tempe, Ariz. Pd was determined by ignition to constant weight. The ignition residue was weighed as palladium(0). Melting points are uncorrected. Ir spectra were obtained on a Perkin-Elmer 621 grating spectrophotometer or (for far-ir) on a Perkin-Elmer Model 180 spectrophotometer. ^{1}H NMR spectra were obtained in $CDCl_3$ solutions using Varian or Perkin-Elmer spectrometers. The 300-MHz ^{1}H NMR spectra were obtained using a Varian HR-300. ^{13}C NMR spectra were obtained using a JEOL PFT PS-100. Chemical shifts (δ) were referenced to TMS. Mass spectra were obtained using a Perkin-Elmer/Hitachi RMU-9D double focusing instrument. Molecular weights were measured using a Mechrolab Osmometer, Model 301 A, operating at 25° for compound **6** and 37° for each of the other measurements. Gas–liquid chromatography (GLC) was done using an Aerograph Model 90 P instrument with the following columns: (1) 5 ft × 0.25 in. 2 Carbowax on Chromosorb P; (2) 10 ft × 0.25 in. Apiezon L on dichlorodimethylsilane treated Chromosorb W. Di-μ-chloro-bis(1,4,5-η-8-methoxycyclooctenyl)dipalladium(II)[26a] and di-μ-chloro-bis(1,4,5-η-8-diethylmalonatocyclooctenyl)dipalladium(II)[7a] were prepared by the literature methods. The ^{1}H NMR spectrum of the 8-methoxy compound has been reported previously;[26f] our results are in agreement (same numbering as in **6**, in $CDCl_3$): δ 6.3–5.75 (1 H, m, H_4 or H_5), 5.75–5.3 (1 H, m, H_5 or H_4), 3.9–3.4 (2 H, m, H_1 and H_8), 3.28 (3 H, s, $-OCH_3$), 3.0–2.4 (2 H, m), 3.4–1.65 (5 H, m), 1.65–1.1 (1 H, m).

***cis,cis*-1,4-Cycloheptadiene.** 1,4-Cycloheptadiene was prepared by a modification of a previously reported method.[15] Reduction of 60 g of cycloheptatriene with 40 g of sodium in 400 ml of ethanol at 0° required 8 hr. The reaction mixture was poured into 1500 g of ice water, followed by saturation with sodium chloride and extraction with three 500-ml portions of pentane. The pentane was washed with 500 ml of H_2O (saturated with sodium chloride), was dried over $MgSO_4$, and was concentrated by atmospheric distillation of the pentane. The residue was added to 100 ml of decalin containing 100 g of maleic anhydride, followed by heating to 80° until cycloheptatriene and cyclohepta-1,3-diene were not detectable in the ^{1}H NMR spectrum. The mixture was then vacuum distilled, and the 53–56° (126 mm) fraction was collected. The mixture (30.5 g) contained 82% 1,4-cycloheptadiene and 18% cycloheptene.

8,8-Dibromobicyclo[5.1.0]oct-3-ene. Using the procedure of Doering and Hoffmann[31] a mixture containing 25 g of 1,4-cycloheptadiene and 5.5 g of cycloheptene in 50 ml of pentane was added to potassium *tert*-butoxide freshly prepared from 8 g of potassium and 100 ml of *tert*-butyl alcohol. Then 50 g of $CHBr_3$ was slowly added to yield 35 g of a mixture containing 8,8-dibromobicyclo[5.1.0]oct-3-ene and 8,8-dibromobicyclo[5.1.0]octane. The products were purified by vacuum distillation, and the fraction distilling at 92–94° (4 mm) was collected.

Bicyclo[5.1.0]oct-3-ene (5). Debromination was accomplished using Gassman's procedure.[32] A mixture (22 g) containing 15 g of 8,8-dibromobicyclo[5.1.0]oct-3-ene was added to 21 g of *tert*-butyl alcohol in 150 ml of tetrahydrofuran followed by 12 g of finely chopped sodium. After refluxing for 4 hr, the reaction mixture was worked up in the usual manner, and the products were vacuum distilled (56–58° (40 mm)) to yield 8 g of a crude mixture of products containing 5.6 g of **5**. The mixture was purified by GLC using column (2) to yield 4.5 g of **5**, The ^{1}H NMR and ir spectra of the isolated **5** are identical with those published for bicyclo[5.1.0]oct-3-ene:[15] ^{1}H NMR, 5.7–5.4 (2 H, m), 2.8–0.5 (9 H, multiplets), 0.12 (1 H, m, H_{endo} on cyclopropyl).

4-Chlorocyclooctene (8). 4-Hydroxycyclooctene[10] (1.2 g, 0.0095 mol) and 3.0 g of pyridine in 25 ml of diethyl ether were cooled in an ice bath. Thionyl chloride (4.8 g, 0.040 mol) was then added dropwise and the solution was stirred for 30 min after addition was completed. The solution was then warmed to 50° for 30 min. Upon cooling, water was added and the ether layer was separated. The water layer was extracted with 50 ml of ether and the ether extracts were combined and washed with water. After drying the ether solution with anhydrous magnesium sulfate the ether was removed. Vacuum distillation produced 1.0 g (73%) of 4-chlorocyclooctene distilling at 86–88° (20 mm): ^{1}H NMR δ 6.1–5.54 (2 H, m, H_1 and H_2), 4.3–3.9 (1 H, m, H_4), 2.62 (2 H, t (J = 7 Hz), H_3 and H_3'—collapses to a 7 Hz doublet on irradiation of either H_4 or H_2), 2.5–1.2 (two 4 H multiplets, $H_{5,5'}$–$H_{8,8'}$). A triplet near δ 2.62 ($H_{3,3'}$, $J \simeq 7$ Hz) was also found in the esters **10** and **17**, below, and is therefore characteristic of the $-CH{=}CHCH_2CHCl-$ grouping in the eight-membered ring. The ir spectrum of **8** run as a thin film on NaCl plates contained the following bands: 3018 (m), 2922 (s), 2850 (m), 1650 (w), 1465 (s), 1445 (m), 1300 (w), 1235 (w), 940 (w), 910 (m), 860 (m), 780 (w), 760 (m), 735 (w), 715 (m), 705 (s), 675 (m).

Di-μ-chloro-bis(1,4,5-η-7-chlorocyclooctenyl)dipalladium(II) (6). $[PdCl_2(PhCN)_2]$ (1.00 g, 0.00261 mol) was dissolved in 15 ml of CH_2Cl_2. **5** (0.282 g, 0.00261 mol) in 2 ml of CH_2Cl_2 was added to the $[PdCl_2(PhCN)_2]$ solution. After a few minutes the color had changed from orange-red to yellow-orange with no precipitation. Then 12 ml of this solution was reduced in volume by evaporation to 2 ml, to which 10 ml of a 50/50 mixture of diethyl ether–hexane was added, precipitating a pale orange powder. (The remaining 5 ml of solution was used in method B of the preparation of **13**, below.) The powder was filtered off and vacuum dried overnight, to yield 0.440 g (86%) of **6**, 147–153° dec. Complex **6** is soluble in most organic solvents. Anal. Calcd for $[C_{16}H_{24}Cl_4Pd_2]$: C, 33.62; H, 4.23; Cl, 24.81; Pd, 37.01; mol wt, 571. Found: C, 33.86; H, 4.04; Cl, 24.20; Pd, 37.34; mol wt (0.0110 *m* in CH_2Cl_2) 558. Ir (KBr, cm^{-1}) 3020 (w), 2930 (s), 2895 (m, sh), 2860 (m), 2820 (m), 1465 (m), 1440 (w), 1425 (w), 1315 (s), 1282 (s), 1210 (s), 1200 (s), 1150 (w), 1112 (w), 1095 (w), 1080 (w), 1030 (m), 1018 (m), 998 (w), 922 (s), 885 (w), 870 (w), 842 (m), 828 (m), 775 (m, sh), 750 (vs), 630 (w), 610 (m), 580 (w); ir (Nujol, cm^{-1}) 458 (m), 375 (w), 351 (m), 325 (w), 286 (s), 224 (s), 210 (s, sh).

Sodium Borohydride Reduction of 6. **6** (0.142 g, 0.000254 mol) in 5 ml of 1,2-dimethoxyethane (dried with 4A molecular sieves) was cooled to −40°. Then 1.0 ml of cyclohexene was added and 0.0095 g (0.0025 mol) of sodium borohydride was then added slowly with stirring. Palladium metal immediately precipitated, but stirring was continued for 90 min longer, at which time 20 ml of water was added. The organic layer was extracted with 50 ml of diethyl ether, washed with water, dried with anhydrous magnesium sulfate, and filtered. GLC analysis of the ether solution showed only one long retention time peak in addition to 1,2-dimethoxyethane and cyclohexene. The solvents were removed by evaporation and the long retention time material was collected by GLC using column (2). Colorless liquid (50 mg, 67%) (**8**) was collected. Anal. Calcd for $C_8H_{13}Cl$: C, 66.45; H, 8.98; Cl, 24.56; mol wt, 144.5. Found: C, 66.33; H, 8.84; Cl, 24.68; molecular ions in the mass spectrum at *m/e* 146 and 144 (^{37}Cl and ^{35}Cl). The ir and ^{1}H NMR spectra were identical with those of 4-chlorocyclooctene prepared from 4-hydroxycyclooctene (above).

Reaction of 6 with Carbon Monoxide in Basic Methanol. Potassium hydroxide (0.105 g, 0.0187 mol) was dissolved in 25 ml of dry methanol. Carbon monoxide was bubbled through this solution for a few minutes before adding 0.570 g (0.00100 mol) of **6**. The bubbling was continued for 5 min, during which time a black precipitate of metallic palladium formed. The palladium was filtered off, water was added, and the solution was extracted with ether. The ether layer was washed with water, dried with anhydrous magnesium sulfate, filtered, and concentrated. The product, ester **10**, was collected by GLC using column (1). This gave 330 mg (82%).

Anal. Calcd for $C_{10}H_{15}O_2Cl$: C, 59.26; H, 7.41; mol wt, 202.5. Found: C, 59.21; H, 7.56; molecular ions in the mass spectrum at *m/e* 204 and 202 (^{37}Cl and ^{35}Cl). ^1H NMR 6.1–5.4 (2 H, m, H_1 and H_2), 4.6–4.2 (1 H, m, H_4), 3.70 (3 H, s, CH_3), 3.2–2.6 (1 H, m, Hα to $-CO_2CH_3$), 2.60 (2 H, t (J = 7 Hz), H_3 and $H_{3'}$), 2.5–1.5 (6 H, m, remaining H's). Double resonance experiments showed that H_3 and $H_{3'}$ are equally coupled to H_2 and H_4 (7 Hz for each coupling), and that the hydrogen α to $-CO_2CH_3$ is not coupled either to the olefinic hydrogens or to H_4. This suggests C_6 or C_7 as the point of ester attachment.

Reaction of 6 with Aqueous Cyanide. 6 (0.80 g, 0.0614 mol) in 10 ml of benzene was shaken with excess aqueous KCN. There was an immediate decoloration of the benzene layer. The benzene layer was separated, washed with water, dried over magnesium sulfate, and concentrated. Only one volatile product was observed by GLC using column (2). This product was collected and identified by its ^1H NMR spectrum, which showed it to be pure **5**. The isolated yield of **5** was 92%.

Acetylacetonato(1,4,5-η-7-chlorocyclooctenyl)palladium(II) (12). 6 (0.325 g, 0.000570 mol) and 0.14 g (0.00115 mol) of sodium acetylacetonate were stirred for 15 min in dry methanol. The methanol was removed and the residue was dissolved in an excess of benzene and filtered. On evaporation of the benzene, crystals appeared which were filtered and washed with pentane. Addition of pentane to the benzene mother liquors gave further precipitate. The two batches were combined to yield 0.30 g of **12** (75%), 112–114° dec. Anal. Calcd for $[C_{13}H_{19}O_2Cl_2Pd]$: C, 44.71; H, 5.49; Pd, 30.47; mol wt, 348. Found: C, 44.64; H, 5.77; Pd, 29.98; mol wt (0.0235 *m* in benzene) 364. ^1H NMR δ 6.45–6.05 (1 H, q ($J \simeq$ 8 Hz), H_4 or H_5), 5.75–5.28 (1 H, q ($J \simeq$ 8 Hz), H_5 or H_4), 5.30 (1 H, s, acetylacetonate methine), 4.9–4.2 (1 H, nonet, couplings similar to 6, H_7), 3.5–3.0 (1 H, m, H_1), 1.95 (6 H, s, acetylacetonate CH_3), 3.0–1.7 (6 H, m), 1.32–0.7 (2 H, m). The ^1H NMR spectrum was unchanged after 20 hr in $CDCl_3$ solution. The multiplet structure at 60 MHz observed for H_4, H_5, H_7, and H_1 and from δ 1.32–0.7 in **12** is practically identical with that for **6** (see results section).

Chloropyridine(1,4,5-η-7-chlorocyclooctenyl)palladium(II) (11). 6 (0.200 g, 0.00035 mol) was treated with 1 ml of pyridine at room temperature. After 15 min diethyl ether (15 ml) was added to complete precipitation. The product was filtered, washed with ether, and vacuum dried. The yield was 0.195 g of pale yellow **11** (76%), 122–125° dec. Anal. Calcd for $[C_{13}H_{17}NCl_2Pd]$: Cl, 19.50; Pd, 29.12; mol wt, 364. Found: Cl, 19.57; Pd, 29.07; mol wt (0.0115 *m* in $CHCl_3$), 329. ^1H NMR δ 8.8–8.55 (2 H, m, py ortho), 7.95–7.6 (1 H, m, py para), 7.5–7.2 (2 H, m, py meta), 6.6–6.1 (1 H, q ($J \simeq$ 8 Hz), H_4 or H_5), 6.0–5.45 (1 H, q ($J \simeq$ 8 Hz), H_5 or H_4), 4.85–4.2)1 H, nonet (coupling similar to 6), H_7), 3.9–3.3 (1 H, m, H_1), 3.0–1.7 (6 H, m), 1.34–0.73 (2 H, m). The multiplet structure in H_5, H_4, H_7, H_1 and from δ 1.34 to 0.73 is nearly identical with that observed in **6** (results section).

Complex **11** rearranges quantitatively over several hours to its allylic isomer **14**. This transformation was monitored by ^1H NMR.

Di-μ-chloro-bis(1-3-η-5-chlorocyclooctenyl)dipalladium(II) (13) Method A. 5 (0.290 g, 0.00268 mol) and 1.4 g (0.00365 mol) of $[PdCl_2(PhCN)_2]$ were refluxed in 20 ml of benzene until the color changed to yellow and precipitation occurred (40 min). The mixture was filtered and the yellow product was washed with diethyl ether and was vacuum dried. The yield of **13** was 0.750 g (98%, based on **5**), 169–170° dec. The product is insoluble in common organic solvents. Anal. Calcd for $C_8H_{12}Cl_2Pd$: C, 33.62; H, 4.23; Pd, 37.34. Found: C, 33.28; H, 3.81; 37.76. Ir (KBr, cm^{-1}): 3018 (w), 2942 (s), 2908 (m, sh), 2841 (w), 1470 (s), 1450 (m), 1297 (w), 1270 (m), 1240 (s), 1065 (w), 1040 (w), 1010 (m), 940 (s), 845 (w), 792 (m), 668 (m); ir (Nujol, cm^{-1}) 494 (w), 432 (w), 390 (w), 370 (w), 354 (m), 330 (w), 282 (w), 262 (s), 242 (m), 222 (w).

Method B. Five milliliters of the CH_2Cl_2 solution taken from the preparation of **6** was allowed to stand at room temperature for 4 days, during which time crystals deposited. The yellow crystals were filtered, were washed with ether, and were vacuum dried to yield 0.140 g (95%), 170–171° dec. The ir spectrum is identical with the method A product.

Reaction of 13 with Carbon Monoxide in Basic Methanol. The procedure was the same as was used in the carbonylation of **6** above. **13** (0.576 g, 0.00101 mol) gave 0.39 g of ester **17** (96%). Anal. Calcd for $C_{10}H_{15}O_2Cl$: C, 59.26; H, 7.41; mol wt, 202.5. Found: C, 59.36; H, 6.98; molecular ions in the mass spectrum at *m/e* 204 and 202 (^{37}Cl and ^{35}Cl). ^1H NMR δ 6.0–5.5 (2 H, m, H_1 and H_2), 4.6–3.9 (1 H, m, H_4), 3.78 (3 H, s, $-CO_2CH_3$), 3.9–3.4 (1 H, m, H_8), 2.63 (2 H, t (J = 7 Hz), H_3 and $H_{3'}$), 2.5–1.5 (6 H, m). Double resonance experiments showed substantial coupling of the olefinic hydrogens to H_8 and also to $H_{3,3'}$. $H_{3,3'}$ is in turn coupled to H_4 ($H_{3,3'}$ collapses to a 7 Hz doublet on irradiation of H_1, H_2, or H_4).

Reaction of 13 with Aqueous Cyanide. 13 (0.080 g, 0.00014 mol) was treated as was 6 with aqueous KCN. The reaction required 5 min of vigorous shaking. The isolation of product was by GLC using column (2), giving 0.030 g (95%) of bicyclo[5.1.0]oct-2-ene, **16**: ^1H NMR δ 6.0–5.2 (2 H, m, H_2 and H_3), 2.5–2.0 (2 H, m, H_4 and $H_{4'}$), 2.0–1.0 (6 H, m), 0.75 (1 H, m), 0.10 (1 H, m, $H_{8\text{-endo}}$). The molecular ion was observed at *m/e* 108 (calcd 108) and the ir spectrum is identical with that published[19] for bicyclo[5.1.0]oct-2-ene.

Acetylacetonato(1,2,3-η-5-chlorocyclooctenyl)palladium(II) (15). 13 (0.140 g, 0.000245 mol) and 0.055 g (0.00045 mol) of sodium acetyl acetonate were stirred for 20 min in 20 ml of dry methanol, during which time all the solid dissolved. The methanol was removed and the residue was taken up in 15 ml of benzene and was filtered. The benzene was concentrated and cooled to give 0.145 g (85%) of **15**, 104–106° dec. Anal. Calcd for $C_{13}H_{19}O_2Cl_2Pd$: C, 44.71; H, 5.49, Pd, 30.47, mol wt, 348. Found: C, 44.99; H, 5.75; Pd, 30.42; mol. wt (0.0320 *m* in benzene), 351. ^1H NMR δ 5.66 (1 H, t (J = 7.8 Hz), H_2), 5.32 (1 H, s, acetylacetonato methine), 4.53 (2 H, q (J = 7.8 Hz), H_1 and H_3), 4.25–3.75 (1 H, m, H_5), 1.97 (6 H, s, acetylacetonato methyl), 3.2–1.1 (8 H, m).

Complex **15** may be converted quantitatively to **13** by treatment with dilute HCl in methanol, from which **13** precipitates. It was also found that **15** gives **16** on treatment with aqueous KCN (89%).

Chloropyridine(1,2,3-η-5-chlorocyclooctenyl)palladium(II) (14). 13 (0.250 g, 0.000439 mol) dissolved readily in 2 ml of pyridine. After filtration the volume was reduced to about 0.5 ml and 10 ml of diethyl ether was added. The resultant precipitate was filtered, was washed with ether, and was vacuum dried, giving 0.265 g of yellow **14** (85%), 136–140° dec. Anal. Calcd for $[C_{13}H_{17}NCl_2Pd]$: C, 42.80; H, 4.67; Cl, 19.50; Pd, 29.12; mol wt, 364. Found: C, 42.81; H, 4.31; Cl, 19.36; Pd, 28.97; mol wt (0.0105 m in $CHCl_3$), 359. ^1H NMR δ 9.0–8.65 (2 H, m, py ortho), δ 8.1–7.6 (1 H, m, py para), 7.6–7.15 (2 H, m, py meta), 5.75 (1 H, t (J = 7.8 Hz), H_2), 4.70 (2 H, q (J = 7.8 Hz), H_1 and H_3), 4.4–3.8 (1 H, m, H_5), 3.2–1.2 (8 H, m). Complex **14** reacts with aqueous cyanide to give a quantitative yield of **16**.

Sodium Borohydride Reduction of 14. The procedure was similar to that used in the borohydride reduction of **6**. Thus 90 mg (0.00025 mol) of **14** was reduced with a reaction time of 2 hr. The only volatile (nonsolvent) product was 4-chlorocyclooctene, **8**, isolated by GLC using column (2) in 50% yield (18 mg).

Reaction of Complex 14 with Carbon Monoxide in Basic Methanol. The procedure was similar to that described for **6**. Thus 0.104 g of complex **14** (0.00028 mol) in 5 ml 0.1 *M* KOH–CH_3OH was treated with carbon monoxide for 25 min (the reaction appeared over in only a few minutes). After work-up, all the nonvolatile residue was taken up in deuteriochloroform. The ^1H NMR showed absorptions identical with those of ester **17** obtained from carbonylation of **13**. Aside from these absorptions and weak pyridine resonances, only trace impurities were observed. The yield of ester **17** from this reaction was estimated by NMR to be nearly 80% (integration with respect to volumetrically added benzene).

The stability of **14** in KOH–CH_3OH in the absence of carbon monoxide was also examined. A solution of 0.076 g of complex **14** (0.21 mmol) in 0.70 ml of 0.3 *M* KOH in CH_3OH was allowed to stand at room temperature for 25 min. Addition of 500 μl of carbon tetrachloride was followed by 500 μl of saturated KCN in D_2O. After shaking, the aqueous layer was removed and the CCl_4 was washed with more D_2O. The ^1H NMR of the CCl_4 layer was practically identical with the NMR of gas chromatographically collected bicyclo[5.1.0]oct-2-ene (**16**) (excepting weak residual pyridine absorption at low field). In particular there was no indication of the presence of 4-chlorocyclooctene, **8**, and only trace $-OCH_3$ absorption (attributed to CH_3OH) was observed. The allyl **14** was therefore judged stable to solvolysis under these conditions.

Preparation of 8-Deuteriobicyclo[5.1.0]oct-3-ene. (a) Debromination of 8,8-Dibromobicyclo[5.1.0]oct-3-ene. The procedure of Osborn[33] was followed. 8,8-Dibromobicyclo[5.1.0]oct-3-ene (10.0 g) was reduced with zinc in glacial acetic acid. After work up and distillation (70–73°, 2.4 mm), 2.0 g of a mixture of *endo*-8-bromobicyclo[5.1.0]oct-3-ene (80%) and *exo*-8-bromobicyclo[5.1.0]oct-3-ene (20%) was obtained. The relative amount of the two isomers was estimated from the ^{1}H NMR spectrum of the mixture (endo >CHBr, δ 3.27 (t, J = 7.4 Hz); exo >CHBr, δ 2.67 (t, J = 3.0 Hz)).

(b) Debromination of 8-Bromobicyclo[5.1.0]oct-3-ene. The debromination was accomplished using a procedure similar to that of Walborsky and Impastato.[34] *n*-Butyllithium (500 μl, 1.8 M) in hexane and 300 μl of dry tetrahydrofuran were mixed under nitrogen. The solution was cooled to −78° and 250 μl of the 80/20 mixture of *endo*- and *exo*-8-bromobicyclo[5.1.0]oct-3-ene was injected through a stopple. The mixture was shaken occasionally and was kept at −78° for 1 hr. Then 200 μl of 99.98% atom pure D_2O was added to the cold (−78°) reaction mixture, which was then warmed with shaking to room temperature. Diethyl ether was added to facilitate separation of layers, and the desired product was separated by GLC using column (2), which gave a total of 50 mg of a mixture of *endo*-8-deuteriobicyclo[5.1.0]oct-3-ene (8) and *exo*-8-deuteriobicyclo[5.1.0]oct-3-ene (20%). The ^{1}H NMR of this mixture is nearly identical with that of **5**, with the exception that the δ 0.12 absorption is diminished to a relative intensity of 0.20 hydrogen, and it appears to be a closely spaced triplet with J ~ 4 Hz. The δ 0.12 resonance is assigned to endo-8-H in the exo-8-D isomer.[35] The mass spectrum of the isolated 80/20 mixture was obtained at 20 eV and it was found that the material was quantitatively deuterated.

The mixture of *endo*-8-deuteriobicyclo[5.1.0]oct-3-ene (80%) and *exo*-8-deuteriobicyclo[5.1.0]oct-3-ene (20%) was used in the reaction with $[PdCl_2(PhCN)_2]$ described in Scheme I.

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Large Metal Ion-Centered Template Reactions. A Uranyl Complex of Cyclopentakis(2-iminoisoindoline)[1]

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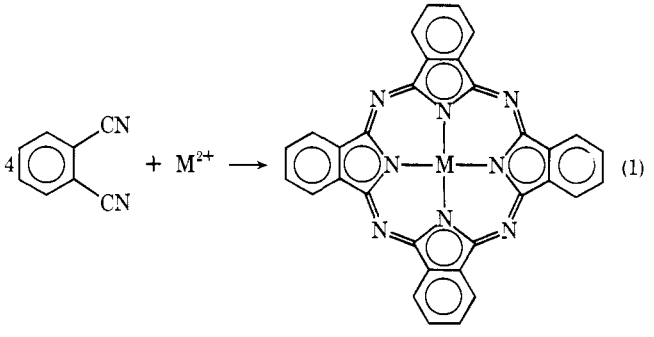
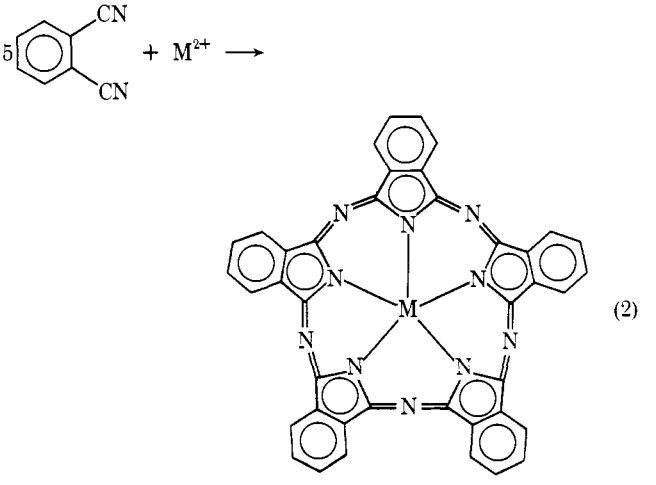
Abstract: The reaction of *o*-dicyanobenzene with anhydrous uranyl chloride *does not* yield a cyclic, four-subunit phthalocyanine complex. Rather, it yields an expanded, cyclic five-subunit pentakis(2-iminoisoindoline) complex—a "superphthalocyanine". Dioxocyclopentakis(2-iminoisoindoline)uranium(VI), $UO_2(N_2C_8H_4)_5$, crystallizes in the monoclinic space group, $P2_{1/c}$, with $a = 8.210$ (3) Å, $b = 21.667$ (7) Å, $c = 18.462$ (5) Å, $\beta = 103.16$ (2)°, and $Z = 4$ ($\rho_{calcd} = 1.891$, $\rho_{obsd} = 1.882$ g/cm^3). Intensity measurements were made for 9564 independent reflections having $2\theta_{Mo\ K\bar{\alpha}} < 60.4°$ at 20 ± 1° with Nb-filtered Mo K$\bar{\alpha}$ radiation on a Syntex $P_{\bar{1}}$ autodiffractometer. The structure was solved using the heavy atom technique. Cycles of anisotropic full-matrix least-squares refinement have given a final value of 0.054 for the conventional unweighted residual, R, for 4709 independent reflections having $I > 3\sigma(I)$. The coordination geometry of the uranium atom approximates an idealized compressed pentagonal bipyramid. The two axial ligands are oxygen atoms with an average U–O bond length of 1.744 (8) Å. The equatorial coordination is by five nitrogen atoms (the average U–N bond length is 2.524 (9) Å) of the 20-atom "inner" ring of the 50-atom (excluding hydrogens) macrocycle. The cyclopentakis(2-iminoisoindoline) ligand is severely and irregularly distorted from planarity, presumably as a consequence of appreciable steric strain within the macrocycle.

Considerable recent interest in coordination chemistry has centered around the role of metal ions as templates in the cyclization and condensation reactions which produce complexes of macrocyclic ligands.[5] A fascinating question related to such reactions is whether increasing the ionic radius of the template will yield an expanded macrocyclic ligand by allowing a greater number of subunits to coordinatively cyclize. In this contribution we present a portion of our work[6] in this area, related to the synthesis of phthalocyanine complexes,[5,7] eq 1, but with the modification that M



(1)

be a far larger[8] actinide ion. For M = UO_2^{2+}, the reaction has been reported and was assumed[9] to yield a normal, tetradentate phthalocyanine complex even though satisfactory analytical data were not obtained. Mass spectral data[10] suggested that five dicyanobenzene subunits might be coordinated to the uranyl ion, and among the various conceivable structural formulations[10,11] is that arising from the reaction given by eq 2. As part of our studies of actinide-centered template reactions, we present here our chemical, spectroscopic, and structural investigations regarding the so-called uranyl phthalocyanine. It is seen that the coordi-



(2)

native preferences of the uranyl ion can dramatically alter the normal course of the cyclization reaction.

Experimental Section

Dioxocyclopentakis(2-iminoisoindolinato)uranium(VI). This compound (formal name, 5,35:14,19-diimino - 7,12:21,26:28,33 - trinitrilopentabenzo [*c,h,m,r,w*][1,6,11,16,21] pentaazacyclopentacosinatodioxouranium(VI)) was prepared by the literature procedure.[9b] Crystals suitable for diffraction studies were grown by slow evaporation of 1,2,4-trichlorobenzene solutions on a hot plate.

Anal. Calcd for $(N_2C_8H_4)_5UO_2$: C, 52.72; H, 2.22; N, 15.37. Found: C, 52.54; H, 2.16; N, 15.21. Calcd for $(N_2C_8H_4)_4UO_2$: C, 49.11; H, 2.06; N, 14.32.

Infrared spectrum (Nujol mull, cm^{-1}): 1505 ms, 1495 ms, 1460 m, 1410 m, 1370 w, 1330 s, 1280 m, 1180 vw, 1165 w, 1110 m, 1070 s, 1025 s, 1013 s, 940 w, 925 s, 897 w, 865 m, 765 m, 715 s, 700 s, 660 w, 625 w.