η^3-Allylpalladium Complexes from Medium-Ring Cycloalkenes

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The dimeric η^3-allylpalladium chloride complexes formed from various cycloalkenes (C_7−C_{13}) and some methyl- and *tert*-butyl-substituted cycloalkenes have been characterized by ^{1}H and ^{13}C NMR spectroscopy and in selected cases by X-ray crystallography. The formation of *syn* and *anti* isomers in the larger ring systems is demonstrated, and complexes with a rearranged ring system are formed from *tert*-butylcyclodecene and *tert*-butylcyclododecene. The sesquiterpene, carophyllene, is shown to form an η^3-allyl exocyclic complex, exclusively from the (*E*)-double bond. Cis and trans isomers, with respect to allyl group orientation in these halo-bridged dimers, have been identified by low-temperature (190K) NMR spectroscopy, and their interconversion ($\Delta G^{\ddagger} \approx 11$ kcal/mol) is considered to involve a "cubic" η^3-allylpalladium chloride tetramer.

Introduction

Allylic activation toward formal nucleophilic substitution may be achieved by utilization of η^3-allylpalladium complexes, either under catalytic or stoichiometric conditions. Numerous applications of this methodology have been reported,[1] with an attraction being the very useful levels of regio- and stereoselectivity that accompany formation and then substitution of the η^3-allyl intermediate. Although medium-ring carbocyclic and heterocyclic derivatives are of increasing importance as synthetic targets, there is very little systematic knowledge of the η^3-allylpalladium derivatives based on these ring systems. A point of particular interest is the possible existence of various *syn* and *anti* η^3-allylpalladium complexes as a function of cycloalkene ring size and how these might regulate the stereochemistry of a substitution product. The possible application of η^3-allylpalladium complexes of medium rings in some synthesis reactions prompted us to prepare and characterize a wide range of such derivatives, which are now discussed.

Palladation of certain cycloalkenes using $PdCl_2$ in aqueous acid was studied by Hüttel,[2] and with cyclohexene and 1-methylcyclohexene, low yields of η^3-allylpalladium complexes were obtained, along with reduction and dehydrogenation products. Subsequently, Trost[3] reported that both alkenes could be palladated in high yield with a procedure utilizing $PdCl_2$−NaCl−NaOAc−$CuCl_2$−HOAc, with careful temperature control. Other studies of the complexes derived from some methyl-substituted cyclohexenes have been reported.[4] The use of palladium(II) trifluoroacetate, $Pd(OCOCF_3)_2$, in η^3-allyl complex formation from alkenes has also been examined,[5] but reactions of cyclohexenes led to disproportionation, and no characterizable products were obtained from cyclopentene and cyclooctene. Hüttel examined[2] the palladation of some higher cycloalkenes and their 1-methyl derivatives and considered the formation of syn and anti isomers from ring systems which, at equilibrium existed as cis−trans olefinic mixtures. Structural ambiguities in some of the derived complexes have been remarked upon.[6]

Results and Discussion

The η^3-allylpalladium complexes to be described were derived, in the most part, (a) cycloalkenes, (b) 1-alkylcycloalkenes, particularly methyl and *tert*-butyl derivatives, and (c) certain 3-methylcycloalkenes. The following discussion is presented on that basis. The procedure involved heating an excess of the cycloalkene with $PdCl_2$ in HOAc until the rapidly formed brown η^2-olefin

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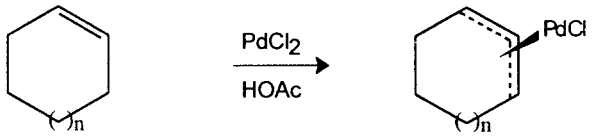

Figure 1.

palladium complex was transformed to the characteristically yellow η^3-allyl complex (Hüttel procedure).[2] Under the temperature and ligand concentration conditions, it is very likely that a thermodynamic distribution of isomeric η^3-allylpalladium complexes is formed.

(a) Cycloalkenes. Complexes derived from cyclohexene and various methylcyclohexenes have been described previously[2−4] and will not be dealt with here except to point out that the Hüttel procedure with cyclohexene (**1**) provides a low yield of the η^3-complex (**6**). However, Trost reports[3] that his procedure is very efficient with this alkene. Hüttel palladation of cycloheptene (**2**) and cyclononene (**4**) affords high yields of the corresponding η^3-palladium complexes, **7** and **9** (Figure 1). However, cyclooctene (**3**) ($n = 3$) and cyclodecene (**5**) ($n = 3$), despite rapidly forming the brown η^2-olefin complexes (generally assumed to be intermediates on the way to the η^3-allyl complexes),[7] were not transformed to **8** and **10**, even after prolonged reaction times. This agrees with the observation of Trost[5] that the usually efficacious, electrophilic $Pd(OCOCF_3)_2$ afforded no characterizable complex from cyclooctene. The η^3-cyclooctenylpalladium bromide dimer has been cited,[8] but to our knowledge, no details of its preparation and properties have been reported.

The synthesis of some acyclic η^3-allyl complexes has been reported by Dent, Long, and Wilkinson.[9] This method, which involves the passage of carbon monoxide through a mixture of allylic chloride and palladium salt dissolved in aqueous methanol, works well for simple acyclic allyl chlorides. Cyclic allylic halides are less well-behaved, and substantial reduction to palladium(0) occurs. In an attempt to acquire the η^3-cyclooctenylpalladium complex (**8**), the Dent conditions were employed using cyclooct-3-enyl chloride, and after chromatography, the complex was obtained in about 26% yield and subsequently characterized by ^{1}H and ^{13}C NMR spectroscopy and X-ray analysis. The resonance of the central carbon (C_2) of **8** was quite broad at *ca.* 30 °C but sharpened at lower temperatures. This led to a more detailed study of the temperature dependence of the ^{1}H and ^{13}C NMR spectra of some of these cyclic η^3-allylpalladium complexes, and this aspect is discussed later.

In view of the apparently irregular NMR behavior and the difficulty in synthesizing the η^3-cyclooctenyl complex (**8**) by the Hüttel procedure, there was a possibility of some unusual structural feature associated with this eight-membered ring complex. Consequently, X-ray structural characterization was undertaken on a single crystal obtained by careful concentration and crystal growth at a dichloromethane−hexane interface. Data were collected at −80 ± 1 °C on a Rigaku AFC6R diffractometer with graphite-monochromated Mo Kα radiation and a rotating anode generator, Table 1. The molecular structure is shown in Figure 2.

Table 1. X-ray Crystallographic Data and Structure Refinement for 7 and 8

	7	**8**
formula	$C_{14}H_{22}Cl_2Pd_2$	$C_{16}H_{26}Br_{0.50}Cl_{1.50}Pd_2$
fw	474.03	524.31
cryst syst	monoclinic	triclinic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	13.366(2)	5.071(1)
b, Å	7.156(1)	7.435(1)
c, Å	17.063(2)	12.271(2)
α, deg		88.50(2)
β, deg	96.04(1)	87.08(2)
γ, deg		78.05(2)
V, Å^3	1623.0(3)	452.0(2)
μ (Mo Kα), cm^{-1}	25.28	33.09
F_{000}	928.00	257
cryst size, mm	0.31 × 0.15 × 0.05	0.38 × 0.16 × 0.02
radiation	Mo Kα	Mo Kα
temp (K)	293 ± 1	193 ± 1
scan type	$\omega-2\theta$	$\omega-2\theta$
2θ range, deg	$39.60 < 2\theta < 46.70$	$44.13 < 2\theta < 52.28$
no. of reflns obsd	2712 ($R_{int} = 0.022$)	2638 ($R_{int} = 0.017$)
no. of params	175	145
GOF	1.76	1.52
R ($I > 2\sigma(I)$)	0.040	0.028
R_w ($I > 2\sigma(I)$)	0.038	0.031
largest diff peak and hole, e Å^{-3}	0.79 and −0.80	1.09 and −0.79

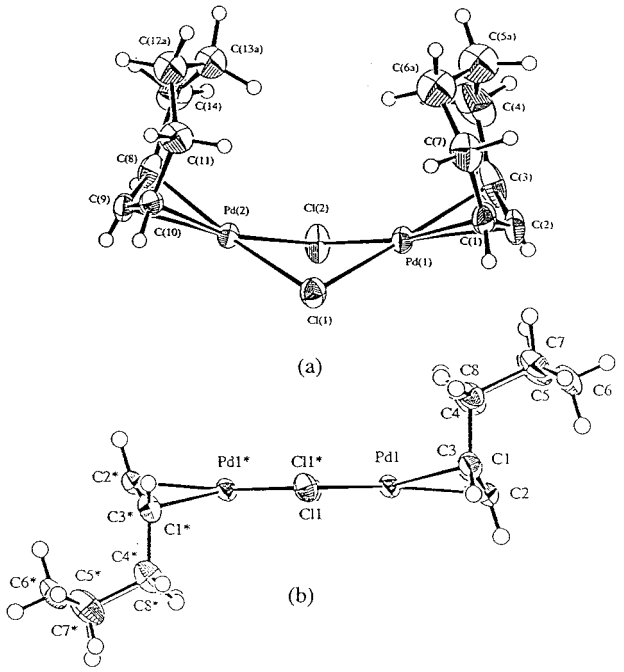

Figure 2. Solid-state molecular structures of (a) di-μ-chlorobis(η^3-cycloheptenyl)dipalladium(II) (**7**) and (b) di-μ-chlorobis(η^3-cyclooctenyl)dipalladium(II) (**8**) as determined by X-ray diffraction.

The X-ray structure of **8** reveals disorder in the halo bridge system, which is discussed in the Experimental Section. This disorder arises from bromide contamination, which probably originated from incomplete solvolysis of 3-bromocyclooctene to the alcohol prior to conversion of the latter to 3-chlorocyclooctene for use in the Dent synthesis. This small amount of bromide was presumably concentrated in the small number of

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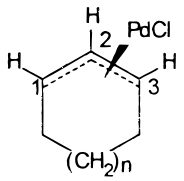
Table 2. ^{1}H and ^{13}C Chemical Shifts for



n	$H_{1,3}$	H_2	$C_{1,3}$	C_2
1	5.16	5.47	78.9	101.8
2	4.93	4.78	84.3	100.9
3	4.77	5.29	79.1	105.0
4	4.65	4.95	81.5	102.9
5	4.60	4.87	83.8	102.1

crystals found suitable for X-ray analysis, but the refinement demonstrates that chloride and bromide may be interchanged, without significant structural perturbation, in the Pd_2X_2 bridge system. This is supported by the work of Brown[10] with structures of mixed-halo dimers of the 2-methylallylpalladium system and the very similar X-ray structures of η^3-cycloheptenylpalladium bromide and chloride dimers, which will be discussed later. The final molecular formula of $C_{16}H_{26}Br_{0.5}Cl_{1.5}$ suggests, on average, one bromide per two dimer molecules, but this does not rule out the presence of some species with a Pd_2Br_2 bridge. The X-ray structure, and NMR data confirm the η^3-allyl structure and define the ring geometry, which would also apply to the pure dichloro-bridged complex.

Acquisition of η^3-cyclodecenylpalladium chloride (**10**) was also attempted by the Dent procedure[9] (as the Hüttel procedure[2] led only to the η^2-cyclodecene palladium complex), and 3-chlorocyclodecene led to a very moderate yield of the required η^3-allyl complex, which was characterized spectroscopically, but suitable crystals for X-ray analysis could not be obtained.

The ^{1}H and ^{13}C NMR chemical shifts for the series of complexes (n = 1−5) are shown in Table 2, and it is clear that the central proton (H_2) resonates at lower field than the terminal protons ($H_{1,3}$), with the exception being the η^3-cycloheptenyl complex (**7**). In all cases, C_2 resonates about 20 ppm to lower field than $C_{1,3}$, but in the η^3-cycloheptenyl complex, C_2 is at the highest field and $C_{1,3}$ at the lowest field for these shifts respectively, within the series. Some years ago it was observed[8] that for the η^3-cycloheptenylpalladium bromide dimer, H_2 resonated at higher field (δ 4.8) than $H_{1,3}$ (δ 5.04), a situation now found for the corresponding chloro complex (**7**). Although explanations of relatively modest variations in chemical shift can be tenuous, we did wonder whether there was a fundamental structural difference between the η^3-cycloheptenyl-complex and the other members of the series, and consequently, an X-ray structural analysis was conducted for the η^3-cycloheptenyl and η^3-cyclononenylpalladium chloride complexes, in addition to the η^3-cyclooctenyl complex, which has been discussed above. The X-ray structure of **7** is shown as Figure 2, with crystallographic data in Table 1.

Generalized representations of *trans*- and *cis*-η^3-allylpalladium chloride complexes are shown in Figure 3 (**I**−**IV**), illustrating both planar (**I, III**) and bent (**II, IV**) Pd_2Cl_2 bridges. Both bridging types have been characterized structurally. Some of these are shown in Table 3,[11−18] with the more common type having a trans arrangement of the η^3-allyl groups and a planar bridge (**I**) with an overall center of symmetry. It appears that there is no example of an η^3-allylpalladium complex with a planar bridge but lacking a center of symmetry at the "center" of the bridge. (Later we discuss the interconversion of the trans and cis dimers in solution).

The important feature to emerge is that the η^3-cycloheptenyl complex (chloro (**7**) or bromo (**20**) bridging), alone of the simpler cyclic systems, adopts the cis-bent bridge arrangement (**IV**) and that the angle between the two palladium coordination planes is 140 ± 1° for both halide systems. This supports the single-site model for the mixed-halide η^3-cyclooctenyl complex described above. Consequently, the unusual order of proton shifts for H_2 and $H_{1,3}$ in the η^3-cycloheptenyl complex is associated with the presence of the bent bridge and not specifically with its composition (i.e., bromo or chloro), provided the structural feature is predominant in solution. Both η^3-allyl, and 1,3-dimethylallylpalladium complexes have significant dipole moments in solution[17] (benzene), and it has been suggested that the weak halo bridges allow bending in solution, with solid-state preferences being regulated by intermolecular forces. This appears to be supported by the considerable range in dihedral angle of the coordination planes in the cis-bent bridge structures listed (125−152°) and the structural preferences of the carene-derived complexes (**15**, **19**).[15] Later, we describe low-temperature NMR spectra of these cyclic η^3-allylpalladium complexes, which require the presence of essentially isoenergetic complexes but which have very similar NMR chemical shifts. These observations are inconsistent with the coexistence of planar and bent-bridge complexes, if the significant chemical shift reversal for the η^3-cycloheptenyl complex (with a bent bridge), relative to those with a planar bridge, is meaningful.

The standard free energies for isomerization of (*E*)-cycloalkenes to (*Z*)-cycloalkenes in acetic acid at 100 °C have been determined,[19] and cycloundecene represents a change over in relative stability of the (*Z*) and (*E*) isomers. These values are (in kcal/mol) −4.04 (cyclononene), −1.86 (cyclodecene), +0.67 (cycloundecene), and +0.49 (cyclododecene). Consequently, it is neces-

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(16) (a) X-ray diffraction analyses on complexes **7** and **8** are described within this publication. (b) X-ray diffraction analyses on complexes **9**, **16**, and **17** reveal a trans-planar arrangement. **9**: Space group $P\bar{1}$; a = 5.064(3) Å, b = 7.340(4) Å, c = 13.364(13) Å; α = 90.82°, β = 94.11(4)°, γ = 103.45(4)°. **16**: Space group $P\bar{1}$; a = 4.8560(8) Å, b = 13.580(2) Å, c = 16.1310(16) Å; α = 113.257(11)°, β = 98.640(10)°, γ = 90.130(10)°. **17**: Space group $P\bar{1}$; a = 7.8016(8) Å, b = 8.4380(10) Å, c = 11.7280(10) Å; α = 70.020(10)°, β = 80.823(8)°, γ = 67.770(10)°. Glenn, M. P.; Rosset, J.-M.; Byriel, K. A.; Kennard, C. H. L.; Kitching, W. Unpublished results.

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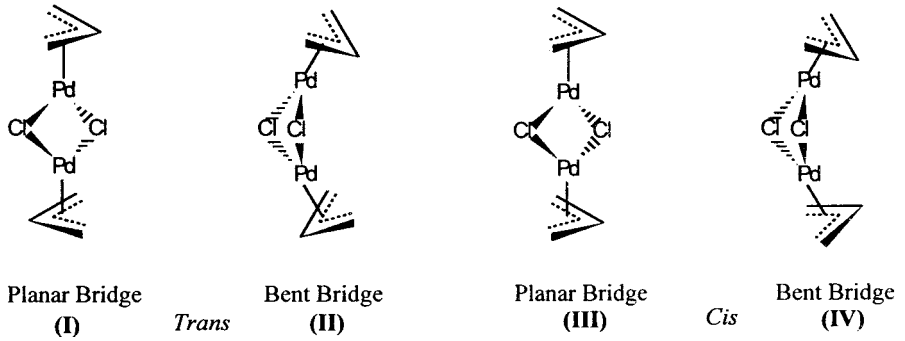
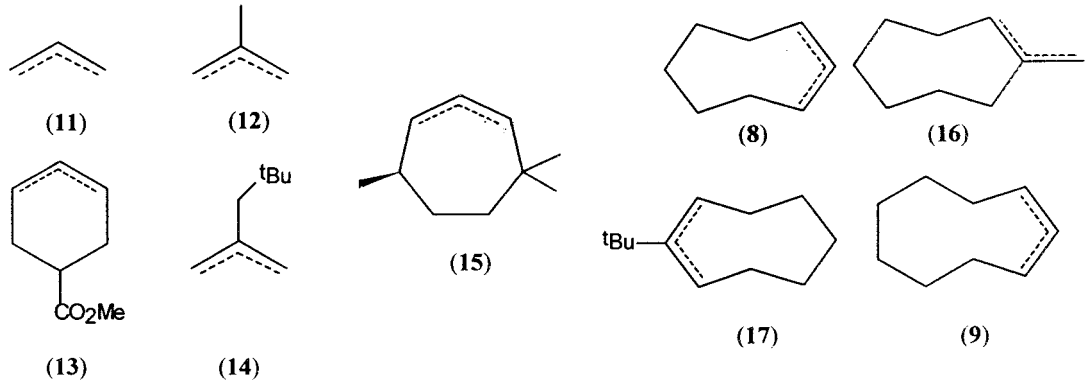


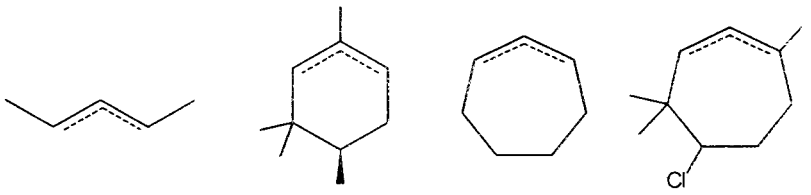
Figure 3.

Table 3. Examples of η^3-Allylpalladium Complexes with Planar and Bent Bridge Systems[a]

complexes of type **I**



complexes of type **IV**



Bridge Angle	150°	130.5°	Br 139° (**20**) Cl 141° (7)	125.2°

[a] No complexes have been reported of type **II** or **III**. References for specific complexes: **11**;[11] **12**;[12] **13**;[13] **14**;[14] **15** and **19**;[15] **7**, **8**, **9**, **16**, and **17**;[16] **18**;[17] **20**;[8] and **13**.[18]

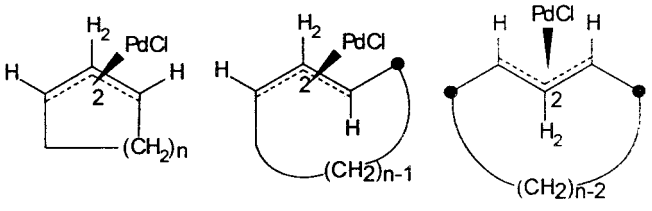


Figure 4. Stereochemistry is referenced to the group at C_2.

sary to consider the formation of *anti*−*syn* (**VI**) and *syn*−*syn* (**VII**) η^3-allyl complexes (Figure 4) in the medium and larger rings, whereas it is clear that the *anti*−*anti* (**V**) arrangement characterizes the C_9 and smaller ring systems. In a sense, the *anti*−*syn* and *syn*−*syn* arrangements are tantamount to the presence of (*Z*,*E*)- and (*E*,*E*)-olefin ring systems, so that energy minimization among interconvertible η^3-allyl isomers will be influenced by normal considerations of transannular effects and torsional strains.

A distinction between arrangements **V**−**VII** can be based on their symmetry (readily reflected by ^{13}C NMR spectra) and the magnitudes of *vic*-$^1H-^1H$ coupling constants, generally clear from the resonance of the central proton (H_2) of the allylic triad. For example, H_2 in **V** experiences two cis-vicinal couplings, whereas H_2 in **VII** experiences two trans-vicinal couplings, and H_2 in **VI** has one of each type. In general, H_2 resonates at lower field than either H_1 or H_3 and the central carbon resonance appears ca. 15−20 ppm to lower field of the terminal carbon signals (see Table 2).[4]

The above considerations are particularly relevant to the mixture of η^3-allyl complexes formed from cycloundecene and cyclododecene. Reaction of cycloundecene (ca. 75:25 *E*:*Z*) with $PdCl_2$ under Hüttel conditions

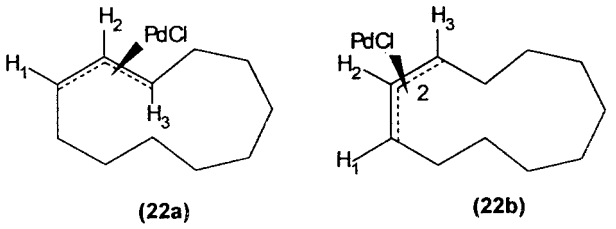


Figure 5.

afforded, in good yield, a mixture of two η^3-allyl complexes with one representing about 95% of the mixture. The central proton H_2 was a clean doublet of doublets (δ 5.15, J = 12.4, 7.1 Hz), ruling out the symmetrical arrangements of types **V** and **VII** for this major isomer. The *anti*−*syn* structure (**22a**), as shown in Figure 5, was confirmed by the distinct signals for H_1 and H_3 at δ 4.13 (J = 11, 6.5, 4.5 Hz) and δ 4.07 (J = 12, 11.5, 2 Hz), respectively.

The above asymmetrical structure is confirmed by the presence of three low-field ^{13}C signals (δ 106.8, 84.2, 74.1) and eight higher-field methylene signals. The minor isomer (~5%) is clearly symmetrical on the basis of a low-field triplet (δ 4.94, J = 8.5 Hz) for H_2 and a symmetrical multiplet for H_1 and H_3 (δ 4.45). These data indicate the *anti*−*anti* structure (**22b**), consistent with the presence of ^{13}C signals at δ 103.0 and 84.1 and four higher field signals.

Palladation of various (*E*,*Z*) mixtures of cyclododecene (**23**) was examined by Hüttel,[2] who concluded that three isomeric complexes (**24a**−**24c**) formed in the ratio 10:50:40, as shown in Figure 6. Palladation of a 2:1 (*E*):(*Z*) mixture of cyclododecene has now been conducted and the structures of the η^3-allyl complexes investigated in detail. Only two and not three isomers are formed, with **24b** and **24c** being ca. 2:1, on the basis of NMR analyses and the symmetry required in the minor isomer (**24c**). Treatment of the isomeric mixture with thallium(I) acetylacetonate in benzene[20] provided a mixture of the pale yellow, very soluble acetylacetonate derivatives **25a** and **25b**, Figure 7, and examination of their ^{1}H and ^{13}C NMR spectra confirmed the conclusions above for the chloro-bridged dimers. The higher field part of the ^{13}C NMR spectrum has 17 resolved signals, with 11 expected from **25a** and 6 from **25b**.

Cyclotridecene was acquired as a 1:1 mixture of (*E*) and (*Z*) isomers, and Hüttel treatment afforded two η^3-allylpalladium complexes, as judged by the ^{13}C NMR spectrum. A symmetrical isomer (~65%) possessed the *syn*−*syn* structure (**26a**), Figure 8, with the minor isomer (~35%) being unsymmetrical (three low-field ^{13}C NMR signals at δ 107.8, 84.1, and 79.0 and a doublet of doublets for H_2 (δ 5.19, $J \approx$ 11.8, 7.3 Hz), and assigned as structure **26b**, analogous to **24b**. The structures assigned for **26a** and **26b** are supported by the number of CH_2 signals at high field, with the five expected being observed for **26a**, and nine of the 10 expected for **26b**.

The η^3-allyl complexes formed from an (*E*)/(*Z*) mixture of cyclotetradecene (ca. 70:30 mixture; ^{13}C NMR δ 131.6 major (*E*), 129.96 minor (*Z*)) were also examined, and a symmetrical complex (**27a**) (~75−80% of the mixture) analogous to **26a** and **24c** is required by the ^{13}C and ^{1}H NMR data summarized below. The second complex (~20−25%; **27b**) is unsymmetrical, analogous to **24b** and **26b**. For **27a**, six higher field ^{13}C signals were located, as expected, whereas for complex **27b**, nine of the anticipated 11 higher-field signals were resolved.

The syn or anti nature of the η^3-allyl complexes formed from the cycloalkenes (C_6−C_{14}) is summarized below. There is a change from the completely *anti*−*anti* arrangement in the C_6−C_{10} systems to a gradual increase in the *anti*−*syn* and ultimately *syn*−*syn* complexes with increasing ring size, Table 4. These trends are consistent with the known free energies for isomerization of cycloalkenes as a function of ring size. In the case of the cyclododecenyl system, originally examined by Hüttel,[2] we find no evidence for the *anti*−*anti* complex, which would experience more significant nonbonding (transannular) effects than the *anti*−*syn* or the *syn*−*syn* isomers.

The pronounced changes in the nature of the η^3-allyl complexes with olefin ring size, as shown in Table 4, are relevant to the results of palladium(0)-catalyzed addition of hexaalkyldistannanes to cyclic allenes.[21] These additions probably proceed through an η^3-allylpalladium intermediate, resulting from oxidative addition of R_6Sn_2 to palladium(0), followed by formation of the η^3-allylpalladium complexes.[22] In the cases of cyclic allenes, possible η^3-allyl complexes are shown in Figure 10 and completion of the reactions would involve delivery of the second $SnMe_3$ group from the palladium-bearing face, providing one diastereomer in the (*Z*) series of distannanes.

The results of the reactions of cyclic allenes of various sizes are summarized in Table 5, and the conditions and characterization of the distannanes are fully described elsewhere.[23] Cyclonona-1,2-diene (n = 1) provides exclusively the (*E*)-vinylic stannane cyclodeca-1,2-diene (n = 2), a mixture of the (*E*) and (*Z*) isomers, whereas the larger allenes cycloundeca-1,2-diene (n = 3) and cyclotrideca-1,2-diene (n =5) yield exclusively the (*Z*) structure. On the basis of the data in Table 4, the *anti*−*anti* complex (**VIII**) is probably exclusively responsible for (*E*)-stannane production for n = 4, but the *syn-anti* complex (**IX**) could, in principle, provide both (*E*)- and (*Z*)-stannanes depending on the regioselectivity of $SnMe_3$ delivery from palladium to the allylic triad. *Syn*−*syn* complex **X** can only provide (*Z*)-stannane and may be dominant in the case with n = 5. The general discussion of ring-size regulation of the geometry of η^3-allylpalladium complexes and their likely intermediacy in the conversion of cyclic allenes to 2,3-bis(trimethylstannyl)-cycloalk-1-enes is of some relevance to the recent report of the cycloisomerization of cyclic allenes bearing pronucleophiles.[25]

***η*³-Allylpalladium Complexes from Methyl and *exo*-Methylene Systems.** Our failure to convert (*Z*)-cyclooctene and (*Z*)-cyclodecene to η^3-allyl complexes by direct palladation suggested that geometrical changes

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(21) Kwetkat, K.; Riches, B. H.; Rosset, J.-M.; Brecknell, D. J.; Byriel, K.; Kennard, C. H. L.; D. J. Young, Schneider, U.; Mitchell, T. N.; Kitching, W. *J. Chem. Soc., Chem. Commun*. **1996**, 773 and references therein.

(22) Mitchell, T. N.; Schneider, U. *J. Organomet. Chem*. **1991**, *407*, 319.

(23) Riches, B. H. Ph.D. Thesis, University of Queensland, 1996.

(24) Wrackmeyer, B. *Ann. Rep. NMR Spectrosc*. **1985**, 73.

(25) Trost, B. M.; Michellys, P.-Y.; Gerusz, V. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1750.

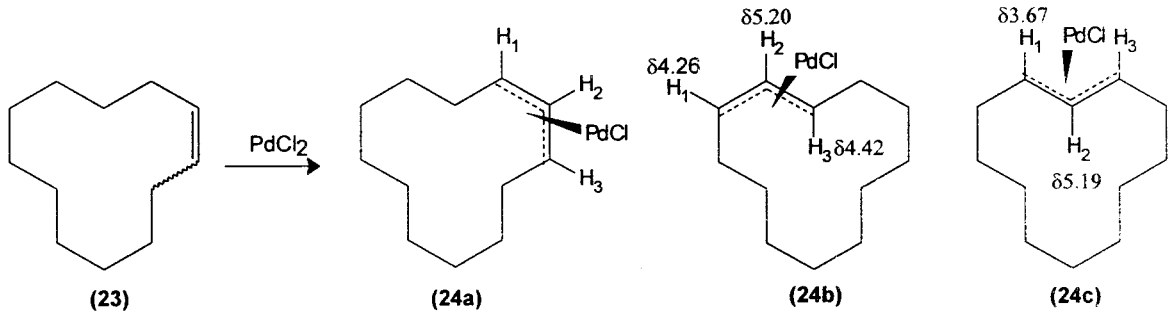


Figure 6.

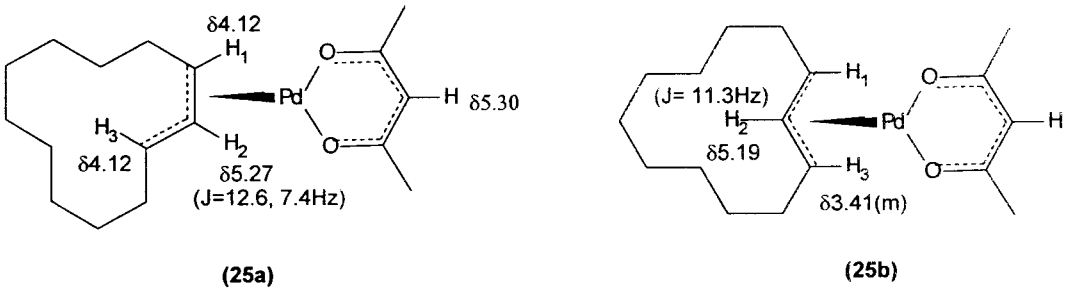


Figure 7.

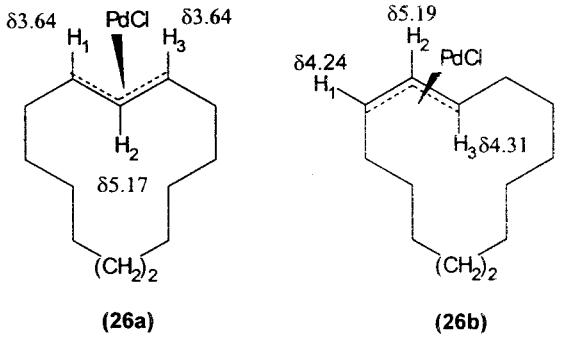


Figure 8.

in the η^2-olefin−palladium(II) complexes, by placement of 1-methyl or 1-*tert*-butyl groups, might have interesting consequences. A number of 1-methylcycloalkenes have been examined previously[4] and some thoroughly reexamined in the present study. Within the 1-methylcycloalkene systems, only 1-methylcyclohexene[3] provides the endo complex (**30**), with others forming exclusively exo complexes. Distinction between these types of complexes is easy, based on the ^{1}H and ^{13}C NMR spectra. Trost has suggested that the *endo*cyclic isomer may be the kinetic product, and attributes the apparently unique behavior of 1-methylcyclohexene to a very favorable orientation of the allylic C−H bond (nearest to CH_3) for insertion. This is shown in Figure 11. (*Z*)-1-Methylcyclooctene and (*Z*)-1-methylcyclodecene, when subjected to Hüttel palladation provide good yields (~75%) of the exo complexes **16** and **33**. In the case of **16** there were six higher field ^{13}C signals, eight for **33**, Table 6. In neither case was there any indication of the formation of symmetrical complex analogous to **30**.

The assignment of syn structures to both **16** and **33** is supported by their similiar ^{1}H and ^{13}C NMR data and the lessened ability of these rings to support a formal (*E*)-double bond, as would be present in the corresponding anti complex. A series of related compounds has been described by Donaldson,[6] who synthesized certain (3-chloro-2-methylenecycloalkyl)palladium chloride complexes by chloropalladation of Ω-methylene-bicyclo-[*n*.1.0]alkenes and subsequent equilibration of the complexes. The data reported for the *syn*-cyclooctenyl complex **34**, *syn*-**35a**, and *anti*-cyclononenyl complexes **35b** and **35c** are shown in Table 7 and support the formulations of **16** and **33**. It is of interest that both the *syn*- and *anti*-cyclononenyl complexes exist at equilibrium in the series **34** and **35a**−**c**, although the syn geometry is preferred. In comparing **16** and **33** with **34** and **35a**−**c** the effects of the 3-chloro substituent must be considered and, consequently, the shifts of the more remote H_2, H_b, and C_2 are most relevant.

An (*E*,*Z*) mixture (55:45) of 1-methylcyclododecene together with methylenecyclododecane was reacted with $PdCl_2$ to form the same η^3-allyl complex formulated previously by Hüttel[2] as the exo complex but of undetermined *syn* or *anti* geometry. This single η^3-allyl complex is formulated as the *syn* complex (**38a**) on the basis of ^{13}C and ^{1}H NMR spectral comparisons with **16** and **33**, Figure 12. Distinctly different ^{1}H NMR shifts, particularly for H_2, would be expected for the *anti* complex (**38b**), on the basis of the trends observed by Donaldson.

The ^{13}C NMR shifts of the allylic triad of **38a** resemble those for the corresponding C_8 and C_{10} complexes (**16** and **33**) and also indicates that an alternative anti arrangement (**38b**) is very unlikely. A suitable crystal for molecular structural determination was not attainable.

The reaction of 3-methylcyclododecene (as a 2:1 (*E*,*Z*) mixture; **39a, 39b**) was briefly examined and afforded

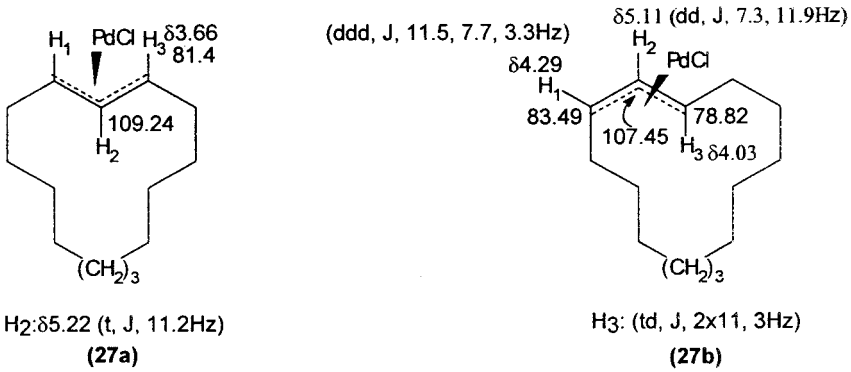


Figure 9.

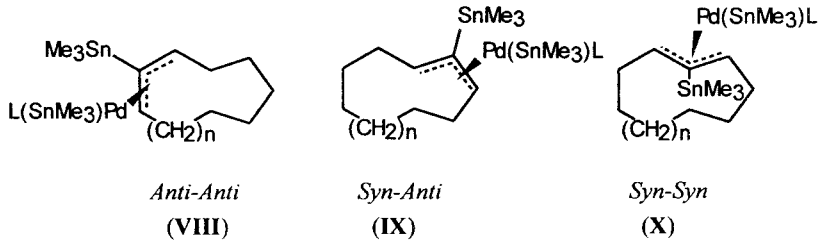
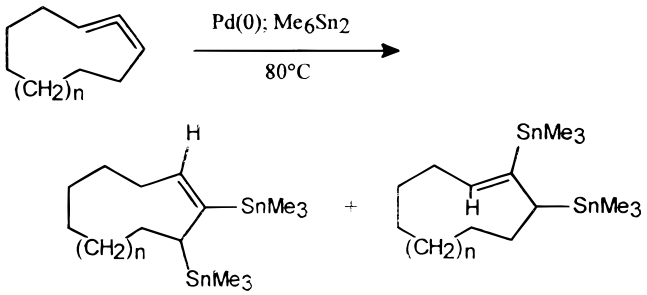


Figure 10.

Table 4. Ring Size and Stereochemistry of η^3-Allylpalladium Complexes

ring size	*anti−anti* type **V**	*anti−syn* type **VI**	*syn−syn* type **VII**
6−10	100	0	0
11	5	95	0
12	0	65	35
13	0	35	65
14	0	20	80

Table 5. Ring Size and Distannane Stereochemistry



product	(*Z*), %	(*E*), %
$n = 1$	0	100 (86 Hz)[a]
$n = 2$	90 (165 Hz)	10 (82 Hz)
$n = 3$	100 (161 Hz)	0
$n = 5$	100 (158 Hz)	0

[a] Values in parentheses are $^3J_{Sn-H}$ values which are diagnostic for (*E*)- and (*Z*)-vinylic stannanes.[21,24]

a mixture of three η^3-allyl complexes, with the major one being **40a**, Figure 13, on the basis of the doublet at δ 5.05 (J = 12 Hz), the CH_3 singlet at δ 1.22, and a second allylic resonance at δ 4.20 (apparent t of d, superimposed on signals from other isomers). ^{13}C NMR signals at δ 78.5, 92.5, and 108.0 and 10 higher field signals between δ 22.15 and 29.84 supported this structure. The *syn−anti* complex (**40b**) showed the expected doublet of doublets at δ 5.15 (dd, J = 7.3, 12.2 Hz) whereas the *syn−syn* complex (**40c**) was characterized by a low-field triplet (δ 5.20, t, J = 10.8 Hz).

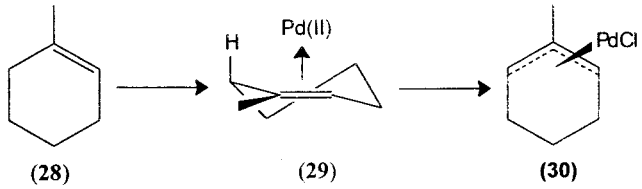
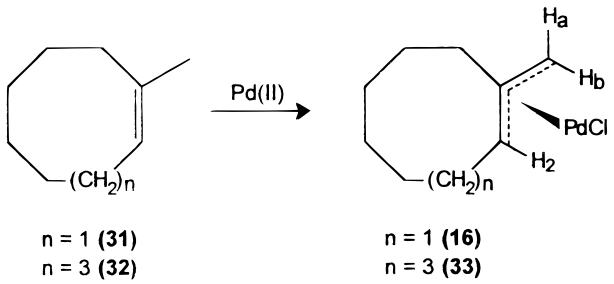


Figure 11.

Table 6. Chemical Shifts of *exo*-η^3-Methylenecycloalkenylpalladium Complexes

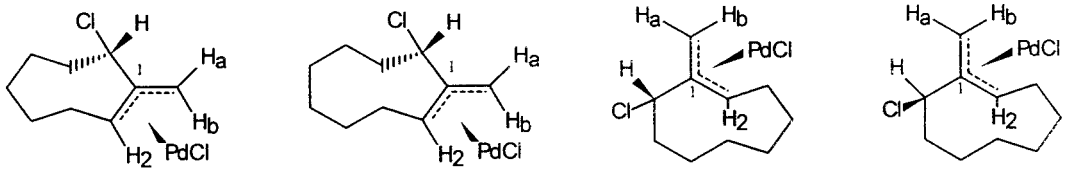


	chemical shift (δ)					
	H_2	H_b	H_a	C_2	C_1	C_{exo}
16	3.48	2.54	3.52	81.2	128.4	59.1
33	3.60	2.60	3.64	84.2	127.9	57.9

Diastereomers of complexes **40b** and **40c** could, in principle, form with the presence of the methyl-bearing stereogenic center, but there was no spectral evidence for this. The relative stereochemistry shown for **40b** and **40c** is likely. Overall, these results from **39a,b** are consistent with the nature of the complexes from cyclododecene itself, with the *anti−anti* complex disfavored, presumably because of transannular nonbonding effects tracing to the presence of the planar cis pentad that incorporates the allylic triad.

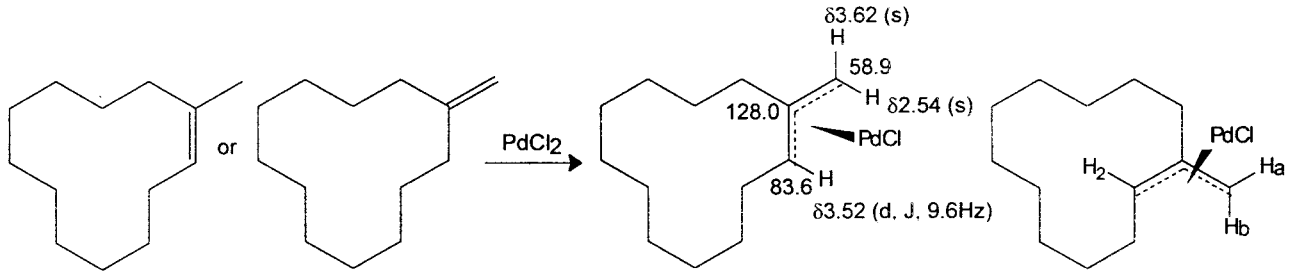
The effect of dimethyl substitution was investigated with (*Z*)- and (*E*)-1,3-dimethylcyclododecenes, obtained

Table 7. Chemical Shifts of *exo*-η^3-*n*-Chloromethylenealkenylpalladium Complexes



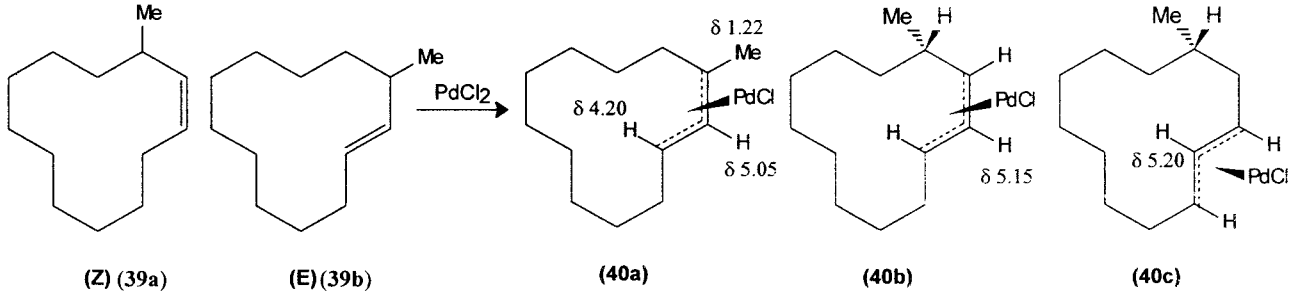
(34) (35a) (35b) (35c)

complex	H_2 (δ)	H_b (δ)	H_a (δ)	C_2 (δ)	C_1 (δ)	C_{exo} (δ)
34	3.58	2.52	4.19	80.5	125.1	55.0
35a	3.72	2.54	4.07	82.0	125.9	53.6
35b	4.33	3.12	4.36	77.8	125.0	63.4
35c	4.80	3.20	3.84			



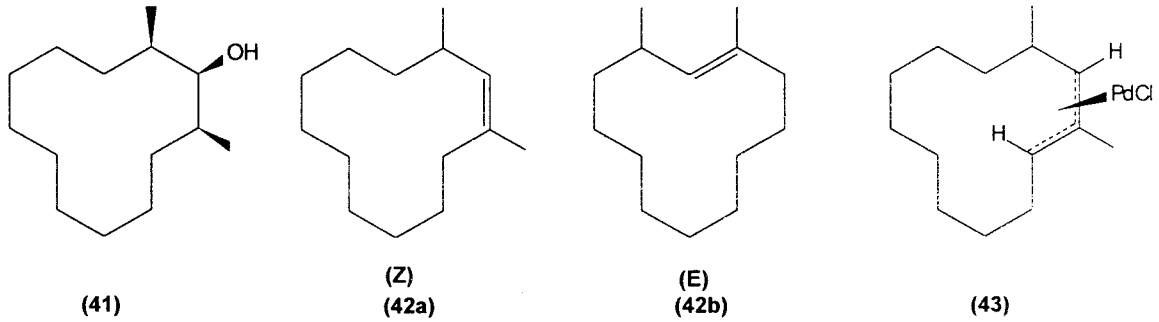
(36) (37) (38a) (38b)

Figure 12.



(Z) (39a) (E) (39b) (40a) (40b) (40c)

Figure 13.



(41) (Z) (42a) (E) (42b) (43)

Figure 14.

by elimination from **41**, Figure 14, acquired by sequential α-alkylation of cyclododecanone followed by reduction.[26] The symmetrical alcohol (^{13}C NMR symmetry) was formulated as **41** on the basis of the narrow triplet for $R_2C\mathbf{H}OH$ (δ 3.29, J = 3 Hz). Conversion of **41** to the mesylate followed by elimination (Et_3N) afforded mainly (*Z*)-alkene **42a**, whereas elimination from the xanthate provided mainly (*E*)-alkene **42b**.

Only **42a** provided a characterizable η^3-allylpalladium complex, formulated as the endo complex (**43**) on the basis of the methyl signals at δ 1.21 (d, $J = 6.3$ Hz) and 2.08 (s) (the latter typical for a 2-CH_3 group in an η^3-allylpalladium complex), with lower field signals at δ 3.82 (d, $J = 10.5$ Hz) and δ 4.22 (t, $J = 7.4$ Hz). The ^{13}C spectrum with signals at δ 117.3, 86.2, and 79.0 (together with 11 higher field signals) is consistent with **43**. The formation of **38a**,**40a**−**c**, and **43** indicates that in the methylcyclododecenyl system, a balance between the formation of exo (e.g., **38a**) and *endo*-complexes (e.g., **43**) has been reached.

Complexes from 1-*tert*-Butylcycloalkenes. 1-Methylcycloalkenes are seen to provide either the *endo*-η^3

(26) Clark Still, W.; Galynker, I. *Tetrahedron* **1981**, *37*, 3981.

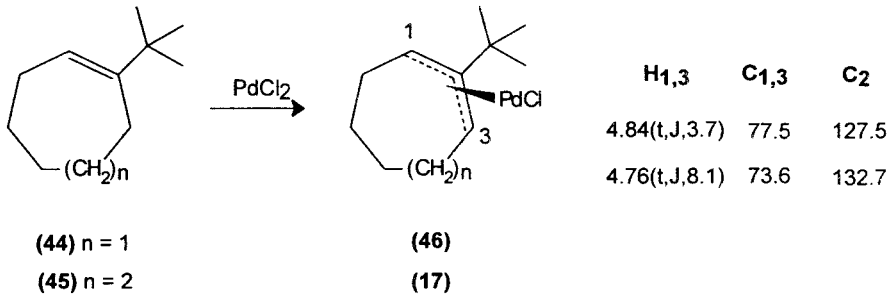


Figure 15.

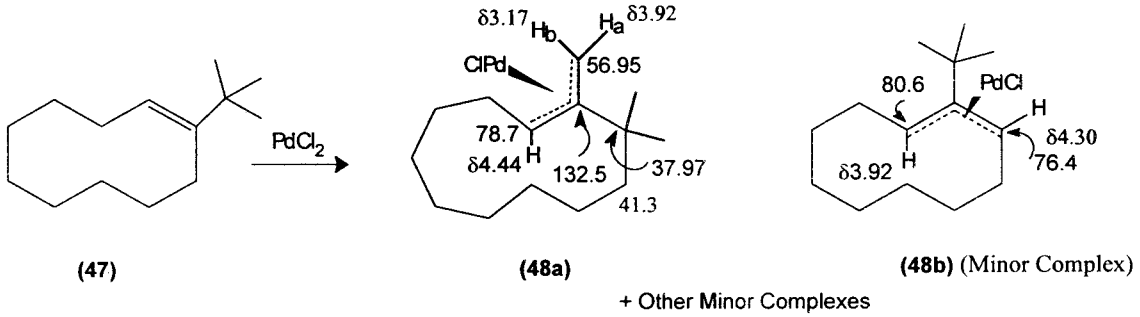


Figure 16.

complexes (for 1-methylcyclohexene and **42a** above) or the more general *exo*-methylene complexes. The *tert*-butyl group may induce sufficient variations in conformation to steer the palladation differently, and in particular, we were interested in the cyclooctyl case, the η^3-allyl complex for which was acquired with difficulty and not by direct palladation.

1-*tert*-Butylcycloheptene and -cyclooctene (**44** and **45**) reacted under Hüttel conditions to afford the *endo*cyclic complexes, whose spectroscopic properties are summarized Figure 15, and which require the symmetrical structures **46** and **17**.

It is of interest that allylic proton loss occurs adjacent to the *tert*-butyl group and not from the apparently more accessible allylic position. This result, when compared with failure of the η^2-complexes of cyclooctene and cyclodecene to transform to the η^3-allyl complexes under conditions so favorable for the corresponding C_7 and C_9 systems, will be considered in terms of the proposal that allylic proton removal occurs by a bridging chloride acting as an internal base.[7,27]

We wondered if this success with *tert*-butylcyclooctene, compared with cyclooctene itself, was associated with a conformational change in the *tert*-butylcyclooctene that better aligned the allylic C−H bond with the π-bond to facilitate proton loss from the η^2-olefin complex and, hence, formation of the η^3-allyl complex. Molecular mechanics calculations (MM3) on this aspect revealed that two conformations of cyclooctene, 1.58 and 3.47 kcal/mol above the minimum energy conformation, had H−C−C=C torsion angles of 119° and 105°, respectively, with this allylic hydrogen on the more exposed π face. In the *tert*-butyl compound, a very favorable H−C−C=C torsion angle of 100° existed in a conformation that was 4.34 kcal/mol above the most favored conformation.[28] These results suggest that the orientation of the allylic C−H bond, by itself, is not the key feature regulating $\eta^2 \rightarrow \eta^3$ complex formation, which may also respond to differences in the palladium−olefin bond strengths. However, competition experiments indicate that cyclooctene is not a significantly better ligand to palladium(II) than cycloheptene.

The reaction of 1-*tert*-butylcyclodecene (**47**) under Hüttel conditions was investigated Figure 16, and examination of the products by ^{13}C NMR spectroscopy indicated a more complex situation than encountered with 1-*tert*-butylcyclooctene. One major (~80%) and probably two minor complexes were formed. Purification of the mixture by HPLC (to remove an oily contaminant) and ^1H and ^{13}C NMR examination of the solid complexes, surprisingly, indicated the major isomer to be of the *exo*-methylene-type on the basis of the characteristic singlets at δ 3.17 and 3.92,and the associated ^{13}C signal at δ 56.95 (DEPT, C−H COSY). A further downfield signal at δ 4.44 (1H, J = 10.5 Hz) is associated with a ^{13}C signal at δ 78.7, with a nonprotonated carbon at δ 132.5, implying adjacent methyl group(s) exerting deshielding β effects. There was no spectral evidence for the presence of an intact *tert*-butyl group in this major complex, formulated as **48a**. This structure requires a ring expansion to the undecane system, and the DEPT spectrum confirms the presence of eight CH_2 groups with the 41.3 ppm signal being unusually deshielded but consistent with the presence of an adjacent *gem*-dimethyl group (β-methyl deshielding). A quaternary carbon (δ 37.97) was identified, and CH_3 signals at δ 30.0 and 24.2 were attributed to the *gem*-dimethyl group, correlating with CH_3 singlets at δ 1.02 and 1.29 in the ^1H NMR spectrum. The *anti* structure of **48a** minimizes nonbonding interactions and is supported by the shift of δ 4.44 for the allylic proton.

Under the reaction conditions ($PdCl_2$, CH_3COOH) it is possible that rearrangement occurs as shown in

(27) Molecular structure data on a relevant series of η^2-cycloalkene platinum(II) complexes will be discussed separately. Glenn, M. Unpublished results.

(28) We are grateful to Dr. D. J. Brecknell for these calculations.

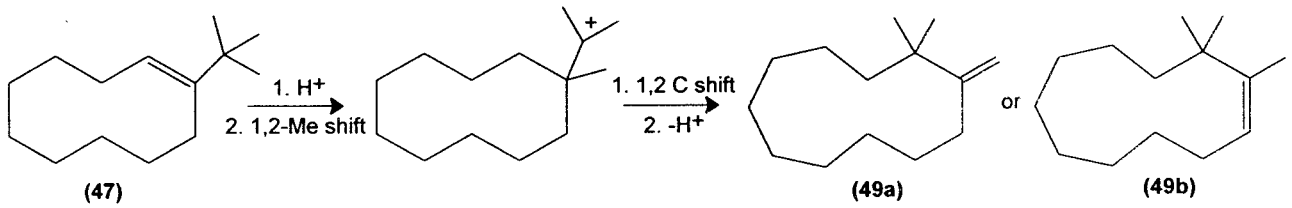


Figure 17.

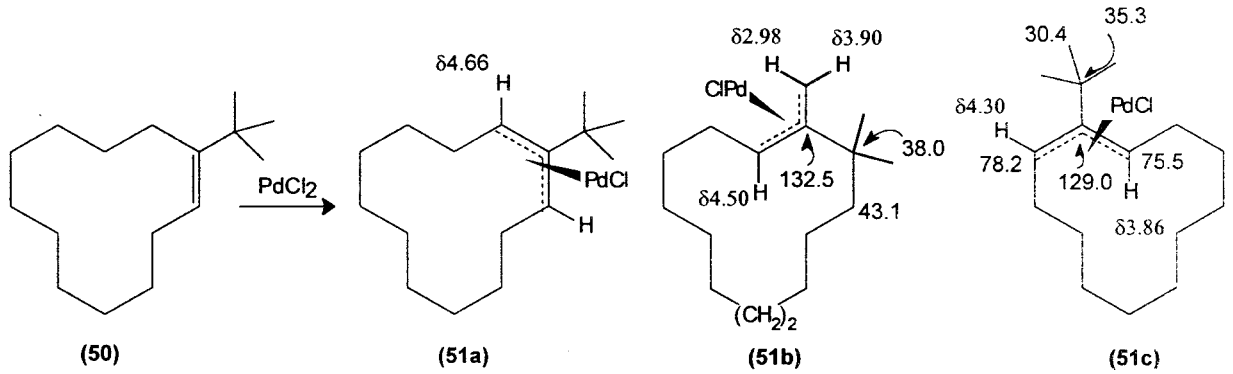


Figure 18.

Figure 17, with either **49a** or **49b** leading to the *exo*-methylene complex **48a**. Complexes of this type are not formed in the cases of *tert*-butylcycloheptene or -cyclooctene and is the minor product in the *tert*-butylcyclododecene case, and these variations presumably reflect the ease of reaching the cyclic cations and the subsequent ring enlargements. The structures of the two minor complexes are not known with certainty. We tentatively suggest structure **48b** for one of these complexes and this is supported by the resemblance of some of its NMR parameters to those of **51c** derived from *tert*-butylcyclododecene. A summary of the NMR data for these minor complexes is located in the Experimental Section.

Palladation of 1-*tert*-butylcyclododecene (**50**) was also examined, Figure 18, and this alkene, as expected, exists as one isomer on the basis of its ^{1}H (δ 5.2, t, J = 8 Hz) and ^{13}C NMR spectra (122.8, 128.3 ppm). One major (~80%) and at least two minor η^3-allylpalladium complexes were formed, with the former being the symmetrical *anti*−*anti* complex (**51a**). Attempts to separate the isomers were not successful.

The symmetry of **51a** is confirmed by the ^{13}C NMR spectrum and the presence of a single low-field proton resonance at δ 4.66 and *tert*-butyl resonance at δ 1.09. The alternative *syn*−*syn* isomer, which is one of the isomers formed from cyclododecene, would appear to incorporate prohibitive nonbonding effects with the *tert*-butyl group. With respect to the minor isomers, one is structurally analogous to the major isomer (**48a**) formed from 1-*tert*-butylcyclodecene and is formulated as **51b**. (In both **48a** and **51b**, the ring is drawn as *anti* but a *syn* geometry cannot be ruled out.) The NMR parameters for **51b** closely resemble those for **48a**. The second minor isomer is formulated as the *syn*−*anti* complex **51c** for the following reasons. A minor methyl signal at δ 30.4 and a quaternary carbon signal at δ 35.3 indicated the presence of a *tert*-butyl group and consequently this isomer was related to the major isomer **51a**. The DEPT spectrum identified 18 resolved CH_2 groups in the high-field portion of the spectrum (in addition to the five prominent CH_2 signals for **51a**), and of these, 10 must be attributed to **51b**, leaving at least eight to be associated with the second minor isomer. The *syn-anti* isomer **51c**, lacking symmetry, should, in principle, exhibit nine CH_2 signals, and we presume one of these minor signals is obscured. Because of the similar relative abundances of **51b** and **51c**, it is not possible to assign groups of CH_2 signals to these isomers. Rearrangement of 1-*tert*-butylcyclododecene (**50**) to the hydrocarbon(s) from which **51b** is derived presumably proceeds as outlined for the 1-*tert*-butylcyclodecene system.

The sesquiterpene carophyllene **52**,[29] which incorporates a nine-membered ring and an (*E*) double bond, reacted efficiently under modified Hüttel conditions to afford, predominantly (~90%), the η^3-allyl complex **53a**, resulting from reaction at the (*E*) double bond. Key NMR data for **53a** are shown in Figure 19.

The ^{1}H and ^{13}C NMR spectra also indicated the formation of a minor, *exo*-methylene η^3-complex, on the basis of singlets at δ 3.2 and 3.75 (η^3-allylpalladium portion) and uncomplexed *exo*-methylene grouping at δ 4.71 and 4.98. The likely structure of this minor complex is **53b**, although we cannot be certain that structures **53a** and **53b** should not be interchanged, although the lower field position of H_2 (δ 4.32) in **53a** compared with its position (δ 4.13) in **53b**, is consistent with the structures, as anti protons, being nearer to the palladium atom, are more strongly shielded.[30] Models indicate that the stereochemistry of palladium relative to the ring junction is as shown.

Variable-Temperature NMR Spectroscopy of η^3-Cycloalkenyl-di-μ-chlorodipalladium(II) Complexes. The broad nature of the resonance for the terminal allyl carbon at ca. 30 °C in the cyclooctenyl complex **8** indicated the operation of a facile dynamic

(29) *Natural Products Chemistry*; Nakanishi, K., Goto, T., Ito, S., Natori, S., Noxoe, S., Eds.; Academic Press: New York, 1974; Vol. 1, p 83.

(30) Maitlis, P. M. *The Organic Chemistry of Palladium*; Academic Press: New York, 1971; Vol. 1, pp 175−252.

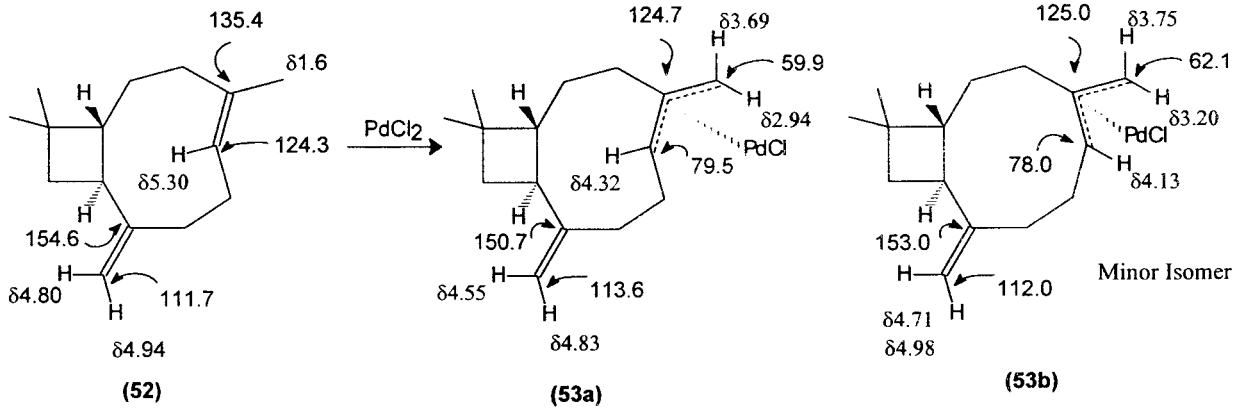


Figure 19.

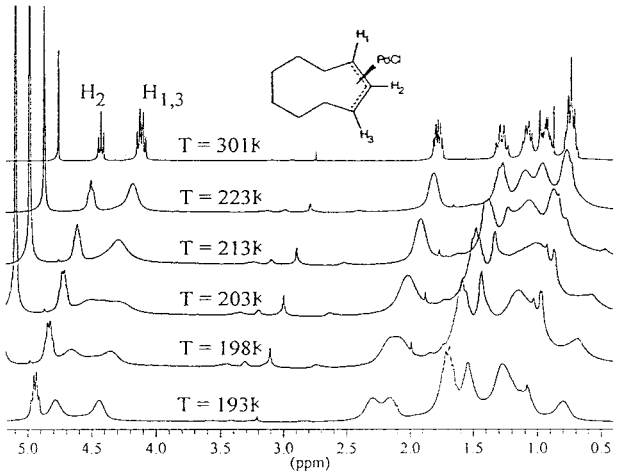


Figure 20. The 400 MHz ^{1}H NMR spectrum of di-μ-chlorobis(η^3-cyclononenyl)dipalladium(II) (**9**) at temperatures from 301 to 192K (solvent CD_2Cl_2). Note, particularly, the temperature dependence of the $H_{1,3}$ resonances.

process, which we thought might be general in these cyclic complexes. Consequently, we carried out variable-temperature NMR investigations on some of these complexes. The cyclononenyl complex (**9**), which we knew was not contaminated by mixed chloro−bromo complexes, as was **8**, was particularly revealing. On cooling a 24 mM solution (CD_2Cl_2 solvent) to 190 K, broadening and eventual splitting of the signal of the terminal allyl protons (initially at δ 4.67) was observed, with new, equi-intense, slightly broadened resonances at δ 4.79 and 4.44 (Figure 20). Coalescence of these signals occurred at ca. 200 K, and using the simple two-site exchange system, this provided a rate constant of 300 s^{-1} with $\Delta G^{\ddagger} = 9.3$ kcal/mol. All higher field resonances were temperature dependent. In particular, the resonance at δ 2.35 (assigned to the ring protons adjacent to the allyl moiety) also separated into two equi-intense signals. The central carbon of the allyl unit (initially at δ 103.4) separated into two equi-intense signals at δ 102.9 and 102.8, and the terminal allylic carbon signal also split into two resonances at δ 83.4 and 79.0 from its initial averaged position at δ 82.0. Other higher field signals were considerably broadened or resolved into equi-intense signals. Similar behavior was exhibited by the *tert*-butylcyclooctenyl complex (**17**), and at 190 K, the *tert*-butyl resonance (δ 1.25, CD_2Cl_2) split into 1:1 resonances at δ 1.18 and 1.13 with coalescence at 255 K, providing $k = 44$ s^{-1} and $\Delta G^{\ddagger} =$ 12.9 kcal/mol. In the ^{13}C NMR spectrum, the terminal allyl carbon resonance (δ 74.1, CD_2Cl_2) split into equi-intense signals at δ 73.3 and 72.9.

The above data indicate the existence of two nearly equienergetic η^3-allylpalladium complexes, with the structural differences being manifested predominantly in the allyl substructure but causing only very modest spectral changes. We considered it unlikely that conformational activity centered on the flexible methylene backbone of these medium rings was responsible, but we did examine the cycloheptenyl complex (**7**), models of which indicated pronounced conformational rigidity. The ^{1}H NMR spectrum of this complex (22 mM, CD_2Cl_2) shows considerable broadening and possible splitting of resonances for the terminal and central protons of the allyl moiety. In the ^{13}C NMR spectrum, the allyl carbon resonances are separated, with the signal at δ101.3 providing equi-intense signals at δ101.9 and 101.8 and the terminal carbon signal (δ 84.7) being resolved into a pair at δ 85.3 and 85.2. These general observations strongly suggested the presence of two η^3-allyl complexes differing in the orientation of the allyl units about the Pd_2X_2 bridge system, with the considerable spatial separation of the allyl groups accounting for the modest differences in both the ^{1}H and ^{13}C NMR parameters and the similar stabilities of the isomers. We then decided to examine the well-studied acyclic complex bis(η^3-2-methylpropenyl)di-μ-chlorodipalladium. When a 24 mM solution of this complex in CD_2Cl_2 was cooled to 200 K, splitting of the methyl resonance (at δ 2.12) into signals at δ 2.07 and 2.05 occurred and that of the anti proton resonance at δ 2.85 into two signals at δ 2.83 and 2.80 whereas the syn resonance merely broadened. The rate constant for averaging was estimated to be 20 s^{-1} with $\Delta G^{\ddagger} \approx 11.6$ kcal/mol. The ^{13}C NMR signals of this complex broaden but do not separate on cooling. The syn and anti proton signals remain quite separate during these processes, so that intervention of σ-allylpalladium species can be discounted.[31]

Concentration effects were briefly explored with the 2-methylallyl complex (**12**). An increase in the dimer

(31) (a) Vrieze, K. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds., Academic Press: New York, 1975. (b) Maitlis, P. M.; Espiret, P.; Russel, M. J. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds., Pergamon: Oxford, U.K., 1982; Vol. 6, p 419. (c) Faller, J. W.; Incorvia, M. J.; Thomsen, M. E. *J. Am. Chem. Soc.* **1969**, *81*, 518.

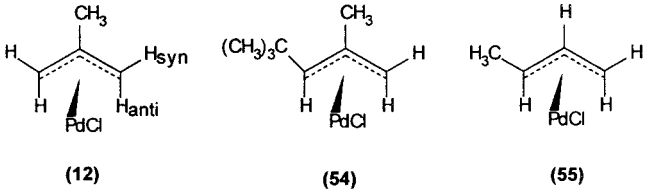


Figure 21.

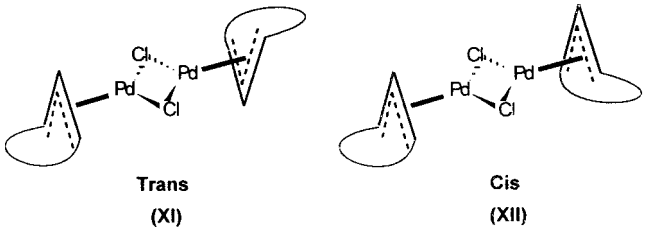


Figure 22.

concentration from 24 to 130 mM resulted in a reduced coalescence temperature (from 224 to 207 K) for the low-temperature components of the methyl proton resonance at δ 2.12, with $\Delta G^{\ddagger}$ reducing from 11.6 to 10.6 kcal/mol. This observation rules out unimolecular dissociation of dimers (followed by recombination) or a rotation of the intact η^3-allyl group but is consistent with the idea of aggregation to a tetramer (second order in dimer).

At about this stage in our investigation, we became aware of some earlier work that described the ^{1}H NMR spectra of several η^3-allylpalladium chloride systems at low temperatures. Van Leeuwin[32] described signal broadening for complex **12** ($CDCl_3$, −88 °C), particularly of the methyl group and anti protons, and also with the *syn*-1-*tert*-butyl-2-methylallyl complex **54**, Figure 21, and considered arrangements with differently oriented η^3-allyl groups. Tibbets and Brown examined by the structures, energetics, and interconversions of mixed-halo dimers of the 2-methylallylpalladium system by ^{1}H NMR and discussed possible intermediates for exchange at the bridge system which would effectively transfer the bridge moiety between allyl groups.[10] This is discussed more fully below. Although X-ray structural analyses of η^3-allylpalladium complexes generally locate the allyl groups trans in the planar-bridged dimer,[18] and cis complexes with bent-halo bridges are known (vide infra), there is the possibility that, in solution, a mixture of cis (**XII**) and trans (**XI**) forms may coexist, and would be anticipated to be of very similar free energies, Figure 22.

This was basically the conclusion of Van Leeuwen,[32] and evidence for such arrangements in η^3-allylpalladium carboxylates,[33] and platinum complexes[34] is available. On this basis, examination of the η^3-crotylpalladium complex **55** would be expected to provide four isomers in solution as shown in Figure 23. Cooling a solution of **55** (180mM, CD_2Cl_2) to 190 K induced broadening of all ^{1}H NMR signals, but no definite resolution was observed. However, the ^{13}C spectrum exhibits clear splitting of the allylic methine carbon resonance (δ 81.8) into four resonances (δ 82.9, 82.8, 82.7, 82.6) of approximately equal intensities, and the methylene carbon

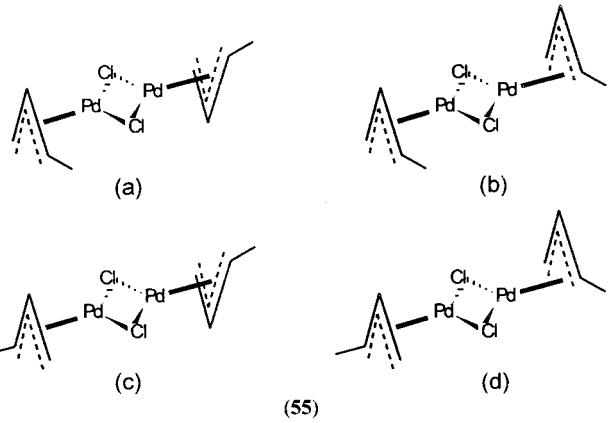
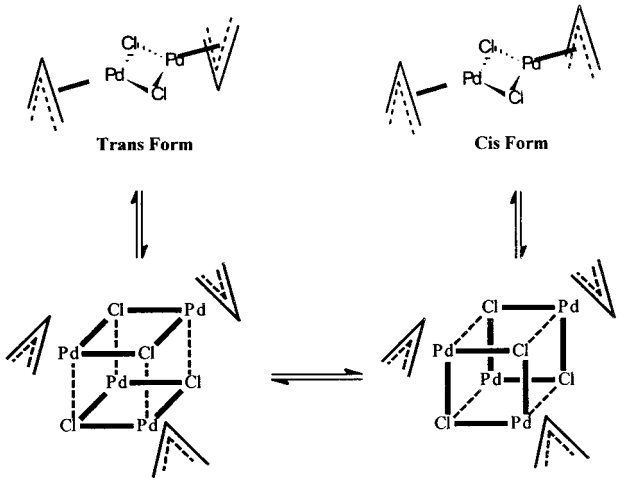


Figure 23.

Scheme 1. Proposed Mechanism for the Conversion of trans to cis η^3-alkenylpalladium Complexes[a]



[a] Fourth allyl unit omitted for clarity.

signal at δ 58.4 separates into two broad resonances at 59.7 and 59.4.

The final point to be addressed concerns the actual pathway for the very facile interconversion of the isomeric dimers such as **XI** and **XII**. Brown's work[10] with mixed-halo-dimers and the present work point strongly to an associative rather than a dissociative step to provide the opportunity for isomer interconversion. Mechanisms based on "flips" and rotations[31c] of allyl groups are contrary to the kinetics and unreasonable on bonding grounds, and consideration of the free energies (and activation energies and entropies where available)[10] supports the view that an intermediate tetramer is involved, such as that shown Scheme 1. Dissociation of the tetramer can then proceed to form dimers in ways that result in relocation of the allyl groups to different bridges and, hence, trans ⇌ cis isomeric interconversion. In the tetramer, there may be some "loosening" of both η^3-allyl bonding as well as Pd−Cl bonding that permits the deformations and slight structural changes[17] required to place the Pd_2Cl_2 bridge optimally with respect to the allyl plane in the forming dimers. With respect to the cyclooctenyl complex **8**, which led to this brief study, we now know that it is a mixed-chloro−bromo complex and it is the only one that did not provide a 1:1 mixture of complexes at low temperatures. However, three dimers were probably

(32) Van Leeuwen, P. W. N. M.; Lukes, J.; Praat, A. P.; Appelman, M. *J. Organomet. Chem.* **1972**, *38*, 199.
(33) Powell, J. *J. Chem. Soc. A* **1971**, 2233.
(34) Mann, B. E.; Shaw, B. L.; Shaw, G. *J. Chem. Soc. A* **1971**, 3536.

present *viz* the dibromo, dichloro, and chloro−bromo, which would not be present on a statistical basis according to the work of Brown.[10] The departure from randomness is relatively slight, however, indicating any three of the halides (Br, I, Cl) can be accommodated in the bridge network without inducing strain. This strongly implies that the X-ray structure described for the cyclooctenyl complex (**8**), which contains a mixed Br−Cl bridge, realistically represents the geometry of the η^3-cyclooctenylpalladium chloride dimer. This is supported strongly by the very similar structural features of the η^3-cycloheptenylpalladium chloride and bromide dimeric complexes discussed earlier.

Experimental Section

All reactions involving organometallic complexes were conducted in dry distilled solvents and carried out under inert atmosphere. Cycloalkenes were prepared by standard methods[35] and exhibited ^{1}H and ^{13}C NMR spectra consistent with their structures.

(*Z*)-1,3-Dimethyl-1-cyclododecene (42a). The procedures described below for the synthesis of **42a** and **42b** are similar to those discussed in ref 25. To a solution of potassium *tert*-butoxide (1.34 g, 12.0 mmol) in THF (50 mL) was added the mesylate of 2,12-dimethylcyclododecanol (3.0 g, 13.34 mmol) in THF (20 mL) dropwise over 15 min. The solution was stirred at room temperature for 1 h before the addition of water (1 mL). The solution was extracted with ether (3 × 50 mL), washed with 2M HCl (2 × 30 mL), and washed with saturated $NaHCO_3$ solution (2 × 30 mL), and the ethereal layer was dried over $MgSO_4$. The solvent was removed under reduced pressure to yield a yellow oil, which was purified by column chromatography (silica 95:5 hexane:ether), yielding a clear oil of **42a** (0.83 g, 41.1%) as a 1:1 mixture of the (*E*) and (*Z*) isomers. Preparative gas chromatography yielded pure (*Z*)-1,3-dimethyl-1-cyclododecene **(42a)** as a clear oil. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 4.17 (t, J = 7.24 Hz, 1H, H_2), 2.08 (s, 3H, Me), 1.80 (m, 3H, $H_{3,12}$), 1.25 (m, 16H, H_{4-11}), 1.20 (s, 3H, Me). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 133.6, 127.5, 35.5, 32.6, 27.5, 26.6, 24.73, 24.70, 24.66, 24.5, 23.8, 23.1, 21.7.

(*E*)-1,3-Dimethyl-1-cyclododecene (42b). To a suspension of sodium hydride (1.44 g, 60 mmol) in ether (100 mL) was added a solution of 2,12-dimethylcyclododecanol (10 g, 47.2 mmol) in ether (30 mL) dropwise over 20 min. The solution was brought to reflux for 3 h and then allowed to cool to room temperature, at which time a solution of carbon disulfide (4.19 g, 55.0 mmol) in ether (10 mL) was added, and the solution was refluxed for a further 3 h. On cooling to room temperature, methyl iodide (7.86 g, 55 mmol) was added and the solution returned to reflux for a further 3 h. The solution was cooled to room temperature, and water (1 mL) was added slowly. The ethereal layer was separated, washed with saturated NaCl solution (3 × 50 mL), and dried over $MgSO_4$, and the solvent was removed under reduced pressure to yield the xanthate of 2,12-dimethylcyclododecanol as a viscous yellow oil. Distillation of the xanthate (82 °C at 0.5 mm Hg) yielded **42b** as a clear oil (5.30 g, 58.2%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 4.85 (d, J = 10.1 Hz, 1H, H_2), 2.50 (m, 1H, H_3), 2.05 (m, 2H, H_{12}), 1.64 (s, 3H, Me), 1.40 (m, 16H, H_{4-11}), 0.89 (s, 3H, Me). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 133.3, 133.0, 36.0, 29.3, 28.1, 24.91, 24.89 (2C), 24.7, 24.5, 23.6, 23.1, 22.9, 22.0.

Procedure A. General Procedure for the Synthesis of Di-μ-chlorobis(η^3-alkenyl)dipalladium(II) Complexes from Alkenes. Di-μ-chlorobis(η^3-cycloheptenyl)dipalladium(II) [$PdCl(C_7H_{11})]_2$ (7). Palladium(II) chloride (510 mg, 2.9 mmol), sodium chloride (330 mg, 5.8 mmol), and sodium acetate (190 mg, 2.9 mmol) were taken up in acetic acid (80 mL) and heated to 85 °C for 2 h, by which time a deep red solution had formed. The solution was cooled to room temperature, and cycloheptene (500 mg, 5.8 mmol) was added. The solution rapidly turned yellow, and after 20 min, the yellow solution was poured into water (50 mL) and extracted with chloroform (3 × 50 mL). The chloroform extracts were dried over magnesium sulfate, and the solvent was removed under reduced pressure to yield **7** as a yellow solid. Drying under vacuum (2 mm Hg, 2 days) yields **7** as a yellow solid (1.07 g, 78.2%). Anal. Calcd for $C_{14}H_{22}Pd_2Cl_2$: C, 35.60; H 4.70%. Found: C, 35.47; H 4.68. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 4.93 (dt, J = 3.32, 8.29 Hz, 2H, $H_{1,3}$), 4.78 (t,[36] J = 8.33 Hz, 1H, H_2), 1.91 (m, 4H, $H_{4,7}$), 1.44 (m, 4H, $H_{5,6}$). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 100.9, 84.3, 33.7, 26.5.

Procedure B. General Procedure for the Synthesis of Di-μ-chlorobis(η^3-alkenyl)dipalladium(II) Complexes from Allyl Chlorides.[9] Di-μ-chlorobis(η^3-cyclooctenyl)-dipalladium(II) [$PdCl(C_8H_{13})]_2$ (8). 3-Chlorocyclooctene (1.0 g, 6.9 mmol), sodium chloride (200 mg, 3.45 mmol), and palladium(II) chloride (303 mg, 1.73 mmol) were combined in methanol (10 mL) containing water (145 μL, 7.9 mmol), degassed, and placed under a carbon monoxide atmosphere. The initial orange suspension turned blood red on exposure to carbon monoxide, and then after several minutes, the solution turned black. The black suspension was left to stir for 2 h at room temperature, by which time a thick deposit of palladium(0) metal was present. The methanol solution was filtered and extracted with chloroform (3 × 10 mL) and dried over magnesium sulfate, and the solvent was removed under vacuum to yield a brownish-orange solid. Column chromatography over alumina (100% chloroform) yielded **8** as a yellow solid (113 mg, 26.2%). The solid was taken up in dry dichloromethane, then hexane was added carefully so to form a second layer above the dichloromethane. Slow evaporation of the solvent yielded crystalline material at the dichloromethane−hexane interface suitable for X-ray crystal structure analysis. Anal. Calcd for $C_{16}H_{26}Pd_2Cl_2$: C, 38.27; H, 5.22%. Found: C, 36.23; H, 5.16. (This low result for C is probably the result of the presence of Br. See Text.) ^{1}H NMR ($CDCl_3$, 200 MHz): δ 5.29 (t, J = 7.92 Hz, 1H, H_2), 4.77 (br q, J = 8.00 Hz, 2H, $H_{1,3}$), 2.35 (m, 2H, $H_{4,8}$), 1.85 (m, 2H, $H_{4,8}$), 1.46 (m, 6H, H_{5-7}). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 105.0, 79.1 (br), 31.2, 25.2, 23.2.

Di-μ-chlorobis(η^3-cyclohexenyl)dipalladium(II) [$PdCl(C_6H_9)]_2$ (6). Reaction of cyclohexene according to procedure **A** yielded **6** as a yellow solid (0.34 g, 32.2%). Anal. Calcd for $C_{12}H_{18}Pd_2Cl_2$: C, 32.32; H 4.07. Found: C, 32.29; H, 4.07. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.47 (t, J = 6.3 Hz, 1H, H_2), 5.16 (m, 2H, $H_{1,3}$), 1.78 (m, 2H, $H_{4,6}$), 1.01 (m, 4H, H_{4-6}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 101.8, 78.9, 28.8, 19.4.

Di-μ-chlorodichlorobis(η^2-cyclooctene)dipalladium-(II) [$PdCl_2(C_8H_{14})]_2$. Reaction of cyclooctene according to procedure **A** yields the olefin complex *di*-μ-chlorodichlorobis-(η^2-cyclooctene)dipalladium(II) as an orange solid (760 mg, 94.3%). Anal. Calcd for $C_{16}H_{28}Pd_2Cl_4$: C, 33.42; H, 4.91%. Found: C, 34.37; H, 5.16. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.18 (q, J = 8.2 Hz, 2H, $H_{1,2}$), 2.32 (br s, 4H, H_{3-8}), 1.60 (m, 4H, H_{4-7}), 1.38 (bs, 4H, $H_{5,6}$). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 109.2, 28.9, 28.7, 26.0.

Di-μ-chlorobis(η^3-cyclononenyl)dipalladium(II) [$PdCl(C_9H_{15})]_2$ (9). Reaction of cyclononene according to procedure **A** yielded **9** as a yellow solid (170 mg, 71.4%). Anal. Calcd for $C_{18}H_{30}Pd_2Cl_2$: C, 40.78; H, 5.70. Found: C, 40.22; H, 5.68. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 4.95 (t, J = 8.2 Hz, 1H, H_2), 4.65 (dt, J = 10.64, 8.33 Hz, 2H, $H_{1,3}$), 2.36 (m, 2H, H_{4-9}), 1.80 (m, 2H, H_{4-7}), 1.58 (m, 4H, H_{4-7}), 1.22 (m, 4H, H_{4-7}). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 102.9, 81.5, 31.2, 27.1, 25.4.

(35) Gardner, P. D.; Narayana, M. *J. Org. Chem.* **1961**, *26*, 3518.

(36) Both the triplet of the central proton and the doublet of triplets for the terminal protons are strongly distorted due to second-order effects (AB system).

Di-μ-chlorodichlorobis(η^2-cyclodecene)dipalladium-(II) [$PdCl_2(C_{10}H_{18})]_2$. Reaction of cyclodecene according to procedure **A** yielded di-μ-chlorodichlorobis(η^2-cyclodecene)-dipalladium(II) as an orange solid (113 mg, 86.0%). Anal. Calcd for $C_{20}H_{36}Pd_2Cl_4$: C, 42.88; H, 6.48. Found: C, 41.85; H, 6.58. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.00 (br s, 2H, $H_{1,2}$), 2.8 (br s, 4H, $H_{3,10}$), 1.20 (m, 12H, H_{4-9}). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 109.3, 29.4, 26.8, 25.4, 21.1.

Di-μ-chlorobis(η^3-cyclodecenyl)dipalladium(II) [$PdCl(C_{10}H_{17})]_2$ (10). Reaction of cyclodecene according to procedure **B** yielded **10** as a yellow solid (34 mg, 8.2%). Anal. Calcd for $C_{20}H_{34}Pd_2Cl_2$: C, 43.03; H, 6.14. Found: C, 42.24; H, 6.02. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.87 (t, J = 8.6 Hz, 1H, H_2), 4.60 (q, J = 8.44 Hz, 2H, $H_{1,3}$), 2.10 (m, 4H, H_{4-10}), 1.59 (m, 8H, H_{5-9}), 1.49 (m, 2H, H_7). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 102.1, 83.8, 28.7, 27.4, 24.5, 20.5.

Di-μ-chlorobis(η^3-cycloundecenyl)dipalladium(II) [$PdCl(C_{11}H_{19})]_2$ (22a and 22b). Reaction of cycloundecene (3:1 trans:cis) according to procedure **A** yielded a yellow solid (1.2 g, 63.0%) composed of the *anti*−*syn* **(22a**; 95%) and the *anti*−*anti* **(22b**; 5%) isomers. Anal. Calcd for $C_{22}H_{38}Pd_2Cl_2$: C, 45.07; H, 5.6.53. Found: C, 44.48; H, 6.59. *Anti*−*syn* **22a**; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.15 (dd, J = 12.4, 7.1 Hz, 1H, H_2), 4.13 (m, 1H, J = 11, 6.5, 4.5 Hz, H_1), 4.07 (m, J = 12, 11.5, 2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 106.8, 84.2, 74.1, 31.8, 28.9, 27.3, 26.3, 24.2, 22.0, 20.7, 20.6. *Anti*−*anti* **22b**; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.94 (t, J = 8.5 Hz, 1H, H_2), 4.45 (ddd, J = 8.50, 6.22, 11.61 Hz, 2H, $H_{1,3}$); ^{13}C NMR ($CDCl_3$ 125 MHz): δ 103.0, 84.1, 30.8, 27.6, 27.0, 20.3, Indiscernible ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.92 (m, 4H, H_4), 1.62 (m, 4H, H_{11}), 1.2 (m, 24H, H_{5-10}).

Di-μ-chlorobis(η^3-cyclododecenyl)dipalladium(II) [$PdCl(C_{12}H_{21})]_2$ (24b and 24c). Reaction of cyclododecene (2:1 trans:cis) according to procedure **A** yielded a yellow solid (2.93 mg, 72.2%) composed of the *anti*−*syn* **(24b**; 65%) and the *syn*−*syn* **(24c**; 35%) isomers. Anal. Calcd for $C_{24}H_{42}Pd_2Cl_2$: C, 46.92; H, 6.89. Found: C, 46.53; H, 7.00. *Anti*−*syn* **24b**: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.20 (dd, J = 13.0, 7.5 Hz, 1H, H_2), 4.42 (m, 1H, H_3), 4.26 (m, 1H, H_1), 2.1−0.9 (m, 18H, H_{4-12}); ^{1}H NMR (C_6D_6, 500 MHz): δ 4.58 (dd, (J = 9.73, 7.24 Hz, 1H, H_2), 4.05 (m, 2H, $H_{1,3}$), 1.95 (m, 1H, H_{4-12}), 1.80 (m, 1H, $H_{4,12}$), 1.70 (m, 1H, $H_{4,12}$), 1.30 (m, 15H, H_{5-11}); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 106.9, 82.6, 77.8, 29.9, 27.8, 26.5, 25.9, 25.6, 24.5, 23.6, 22.6, 22.4. *Syn*−*syn* **(24c)**: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.19 (t, J = 11.9 Hz, 1H, H_2), 3.67 (m, 2H, $H_{1,3}$), 2.1−0.9 (m, 18H, H_{4-12}); ^{1}H NMR (C_6D_6, 500 MHz): δ 4.71 (t, J = 11.37 Hz, 1H, H_2), 3.28 (m, 2H, $H_{1,3}$), 1.76 (m, 2H, $H_{4,12}$), 1.51 (m, 2H, $H_{4,12}$), 1.30 (m, 14H, H_{5-11}); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 109.3, 80.3, 30.8, 26.5, 26.4, 25.9, 25.8, 25.2.

Acetylacetonato(η^3-cyclododecenyl)palladium(II) ($C_5H_7O_2$)($C_{12}H_{21}$)Pd (25a and 25b). To a suspension of **24b,c** in dry benzene (530 mL) under a nitrogen atmosphere was added thallium(I) acetylacetonate (1.0 g, 3.02 mmol). The suspension was heated to 50 °C and stirred for 1 h, by which time a white precipitate of thallium chloride had formed. The white precipitate was removed by filtration, and the solvent was removed from the resulting yellow solution under reduced pressure to yield a yellow solid. The crude solid of **25a,b** was recrystallized from toluene:hexane (5:1; 20 mL) to yield **25a,b** as a pale yellow solid (874 mg, 78.1%). Anal. Calcd for $C_{17}H_{28}PdO_2$: C, 55.06; H, 7.61%. Found: C, 54.47; H, 7.67. *Anti*−*syn* **25a:** ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.30 (s, 1H, OCC**H**CO), 5.27 (dd, J = 12.6, 7.4 Hz, 1H, H_2), 4.12 (m, 2H, $H_{1,3}$), 1.92 (s, 6H, CH_3), 1.90−1.00 (m, 18H, H_{4-12}); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 202.0, 108.2, 99.9, 73.4, 71.2, 29.0, 28.3, 27.5, 26.7, 26.4, 26.0, 25.2, 24.5; 22.8; 22.5. *Syn*−*syn* **25b**: ^{1}H NMR ($CDCl_3$, 200 MHz): δ 5.30 (s, 1H, OCC**H**CO), 5.19 (t, J = 11.3 Hz, 1H, H_2), 3.41 (m, 2H, $H_{1,3}$), 1.92 (s, 6H, CH_3), 1.90−1.00 (m, 18H, H_{4-12}). ^{13}C NMR ($CDCl_3$ 50 MHz) δ 201.0, 110.5, 99.8, 72.0 30.4; 28.4; 28.1; 25.8; 24.9; 23.7.

Di-μ-chlorobis(η^3-cyclotridecenyl)dipalladium(II) [$PdCl(C_{13}H_{23})]_2$ (26a and 26b). Reaction of cyclotridecene (1:1 trans:cis) according to procedure **A** yielded a yellow solid (1.23 g, 68.0%) composed of the *syn*−*syn* **(26a**; ∼65%) and the *syn*−*anti* **(26b)** (∼35%) isomers. Anal. Calcd for $C_{26}H_{46}Pd_2Cl_2$: C, 48.61; H, 7.22. Found: C, 48.56; H, 7.36. *Syn*−*syn* **26a**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.17 (t, (J = 11.05 Hz, 1H, H_2), 3.64 (br td J = 2 × 10.6, 3.6 Hz, 2H, $H_{1,3}$), 1.88 (m, 2H, $H_{4,13}$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 109.5, 82.0, 32.6, 27.2, 26.9, 26.3, 25.4. Syn−anti **26b**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.19 (dd, (J = 11.8, 7.3 Hz, 1H, H_2), 4.31 (td, (J = 2 × 11.3, 4.0 Hz, 1H, H_3), 4.24 (dd, (J = 11.6, 8.0, 3.0 Hz, 1H, H_1), 2.0 (m, 1H, $H_{4\ or\ 13}$), 1.88 (m, 1H, $H_{4\ or\ 13}$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 107.8, 84.1, 70.0, 33.8, 27.7, 27.6, 27.5, 27.0, 26.7, 24.3, 23.5, 22.1; Indiscernible ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.51 (m, 16H, $H_{4,13}$), 1.30 (m, 24H, $H_{4,13}$).

Di-μ-chlorobis(η^3-cyclotetradecenyl)dipalladium(II) [$PdCl(C_{14}H_{25})]_2$ (27a and 27b). Reaction of cyclotetradecene (2:1 trans:cis) according to procedure **A** yielded a yellow solid (2.62 g, 69.3%) composed of the *syn*−*syn* **(27a**; ∼80%) and the *syn*−*anti* **(27b**; ∼20%) isomers. Anal. Calcd for $C_{28}H_{50}Pd_2Cl_2$: C, 50.16; H, 7.52. Found: C, 50.15; H, 7.65. *Syn*−*syn* **27a**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.22 (t, J = 11.2 Hz, 1H, H_2), 3.66 (m, 2H, $H_{1,3}$); ^{13}C NMR ($CDCl_3$ 125 MHz) δ 109.2, 81.4, 30.0, 26.8, 26.7, 25.8, 25.5, 25.4. Syn−anti **27b**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.11 (dd, J = 11.9, 7.30 Hz, 1H, H_2), 4.29 (ddd, J = 11.5, 7.7, 3.3 Hz, 1H, H_1), 4.03 (td, J = 11.0, 11.0, 3.0 Hz), 1H, H_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 107.5, 83.5, 78.8, 32.3, 28.1, 27.9, 27.3, 27.0, 26.8, 26.2, 25.3, 25.0; Indiscernible ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.04−1.30 (m, 44H, $H_{4,14}$).

Di-μ-chlorobis(*exo*-η^3-1-methylenecyclooctenyl)dipalladium(II) [$PdCl(C_9H_{15})]_2$ (16). Reaction of 1-methylcyclooctene according to procedure **A** yielded **16** as a yellow solid (1.23 g, 58.2%). Anal. Calcd for $C_{18}H_{30}Pd_2Cl_2$: C, 40.78; H, 5.70. Found: C, 40.22; H, 5.69. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.52 (s, 1H, H_a), 3.48 (dd, J = 14.7, 9.8 Hz, 1H, H_2), 2.54 (s, 1H, H_b), 2.10 (m, 2H, H_{3-8}) 1.90 (m, 2H, H_{3-8}), 1.50 (m, 8H, H_{4-7}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 128.4, 81.2, 59.1, 31.3, 30.6, 28.3, 28.0, 26.2, 25.8.

Di-μ-chlorobis(*exo*-η^3-1-methylenecyclodecenyl)dipalladium(II) [$PdCl(C_{11}H_{19})]_2$ (33). Reaction of 1-methylcyclodecene according to procedure **A** yielded **33** as a yellow solid (0.82 g, 53.5%). Anal. Calcd for $C_{22}H_{38}Pd_2Cl_2$: C, 45.07; H, 6.53%. Found: C, 45.07; H, 6.75. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.64 (s, 1H, H_a), 3.60 (d, J = 10.0 Hz, 1H, H_2), 2.60 (s, 1H, H_b), 2.30 (dt, J = 21.0, 7.25 Hz), 2H, $H_{3,10}$), 2.10 (m, 2H, H_{3-10}), 1.60 (m, 12H, H_{4-9}). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 127.9, 84.2, 57.9, 30.1, 30.0, 26.6, 26.4, 26.3, 25.5, 21.1, 20.7.

Di-μ-chlorobis(*exo*-η^3-1-methylenecyclododecenyl)dipalladium(II) [$PdCl(C_{13}H_{23})]_2$ (38a). Reaction of a mixture of (*E*)- and (*Z*)-1-methylcyclododecene and methylenecyclododecane according to procedure **A** yielded a yellow solid (2.65 g, 58.7%) of **38a**. Anal. Calcd for $C_{26}H_{46}Pd_2Cl_2$: C, 48.61; H, 7.22. Found: C, 48.54; H, 7.10. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.62 (s, 1H, H_a), 3.52 (d, J = 9.6 Hz, 1H, H_2), 2.54 (s, 1H, H_b), 2.05 (m, 2H, H_{3-12}), 1.94 (m, 2H, $H_{3,12}$), 1.35 (m, 16H, H_{4-11}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 128.0, 83.6, 58.9, 29.7, 29.5, 27.3, 26.2, 25.8, 25.7, 25.5, 25.1, 22.8, 22.3.

Di-μ-chlorobis(*exo*-η^3-2-methylcyclododecenyl)dipalladium(II) (40a) and Di-μ-chlorobis(η^3-4-methylcyclododecenyl)dipalladium(II) [$PdCl(C_{13}H_{23})]_2$ (40b and 40c). Reaction of 3-methylcyclododecene (2:1 *trans:cis*) according to procedure **A** yielded a yellow solid (0.785 g, 44.2%) composed of *syn*−*anti* **(40a)**, *syn*−*anti* **(40b)** and the *syn*−*syn* **(40c)** isomers. Anal. Calcd for $C_{26}H_{46}Pd_2Cl_2$: C, 48.61; H, 7.22. Found: C, 48.55; H, 7.24. *Syn*−*anti* **40a:** ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.05 (d, J = 12 Hz, 1H, H_2), 4.20 (dt, J = 12.1, 6.9 Hz, 1H, H_2), 1.22 (s, 3H, Me), 1.7−0.6 (m, 18H, H_{4-12}); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 108.0, 92.5, 78.5, 32.3, 29.8, 26.4, 25.9, 25.6, 24.2, 23.6, 23.5, 22.3, 22.1. *Syn*−*anti* **40b** ^{1}H NMR ($CDCl_3$,

200 MHz) δ 5.15 (dd, J = 7.3, 12.2 Hz, 1H, H_2), 4.63 (dd, J = 12.9, 5.2 Hz, 1H, H_1), 3.39 (dd, J = 12.0, 8.8 Hz, 1H, H_3), 1.7−0.6 (m, 20H, H_{4-12}). *Syn*−*syn* **40c**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.20 (t, J = 10.8 Hz, 1H, H_2), 3.98 (dd, J = 10.8, 7.2 Hz, 1H, H_3), 3.50 (br t, J = 10.3 Hz, 1H, H_1), 1.7−0.6 (m, 20H, H_{4-12}). **40b** and **40c**: ^{13}C NMR ($CDCl_3$, 50 MHz) δ 105.6, 101.6, 84.2, 82.3, 79.5, 77.9, 38.2, 38.1, 35.3, 35.2, 34.5, 34.1, 32.8, 32.7, 30.2, 29.6, 27.2, 26.8, 26.1, 25.4, 25.2, 25.1, 25.0, 24.5, 22.7, 21.1.

Di-μ-chlorobis(*endo*-η^3-2,4-dimethylclododecenyl)dipalladium(II) [PdCl($C_{14}H_{25}$)]$_2$ (43). Reaction of (*Z*)-1,3-dimethylclododecene according to procedure **A** yielded **43** as a yellow solid (0.32 g, 34.1%). Anal. Calcd for $C_{28}H_{50}Pd_2Cl_2$: C, 50.16; H, 7.52. Found: C, 50.06; H, 7.70. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 4.22 (t, J = 7.4 Hz, 1H, H_{12}), 3.82 (d, J = 10.5 Hz), 1H, H_2), 2.08 (s, 3H, Me(C_2)), 1.3 (m, 17H, H_{3-11}), 1.21 (d, J = 6.3 Hz, 3H, Me(C_4)). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 117.3, 86.2, 79.0, 36.2, 32.5, 26.5, 26.1, 26.0, 25.3, 25.1, 23.8, 22.9, 22.2, 20.1.

Di-μ-chlorodichlorobis(η^3-2-*tert*-butylcycloheptenyl)dipalladium(II) [PdCl($C_{11}H_{19}$)]$_2$ (46). Reaction of 1-*tert*-butylcycloheptene according to procedure **A** yielded **46** as a yellow solid (1.24 g, 69.0%). Anal. Calcd for $C_{22}H_{38}Pd_2Cl_2$: C, 45.07; H, 6.53. Found: C, 45.07; H, 6.75. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 4.84 (t, J = 3.7 Hz, 2H, $H_{1,3}$), 2.17 (m, 2H, $H_{4,7}$), 1.85 (m, 2H, $H_{4,7}$), 1.40 (m, 4H, H_{5-6}), 1.12 (s, 9H, ^{t}Bu). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 127.5, 77.5, 36.5, 34.0, 31.0, 27.2.

Di-μ-chlorodichlorobis(η^3-2-*tert*-butylcyclooctenyl)dipalladium(II) [PdCl($C_{12}H_{21}$)]$_2$ (17). Reaction of 1-*tert*-butylcyclooctene according to procedure **A** yielded **17** as a yellow solid (103 mg, 59.0%). Anal. Calcd for $C_{24}H_{42}Pd_2Cl_2$: C, 46.92; H, 6.89. Found: C, 46.92; H, 7.13. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 4.76 (t, J = 8.1 Hz, 2H, $H_{1,3}$), 2.40 (m, 2H, $H_{4,8}$), 1.95 (m, 2H, $H_{4,8}$), 1.36 (m, 6H, H_{5-7}), 1.19 (s, 9H, ^{t}Bu). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 132.7, 73.6, 36.0, 31.1, 30.9, 26.0, 23.3.

Di-μ-chlorobis(*exo*-η^3-2-methylene-3,3-dimethylcycloundecenyl)dipalladium(II) (48a) and Di-μ-chlorodichlorobis(η^3-2-*tert*-butylcyclodecenyl)dipalladium(II) (48b) [PdCl($C_{14}H_{25}$)]$_2$. Reaction of *tert*-butylcyclodecene according to procedure **A** yielded a yellow solid (0.74 g, 62.8%) composed of **48a** (~80%) and two minor isomers structurally similar to **48b**. Anal. Calcd for $C_{14}H_{50}Pd_2Cl_2$: C, 49.94; H, 7.47. Found: C, 49.34; H, 7.23. **48a**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.44 (d, J = 10.5 Hz, 1H, H_{11}), 3.92 (s, 1H, H_a), 3.17 (s, 1H, H_b), 1.5−1.0 (m, 16H, H_{4-11}), 1.29 (s, 3H, Me), 1.02 (s, 3H, Me); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 133.5, 78.7, 57.0, 41.3, 38.0, 30.5, 30.0, 29.1, 27.4, 26.8, 25.4, 25.2, 24.2, 20.9. **Minor isomer (48b) A:** ^{1}H NMR δ 3.43 (br d, J = 9 Hz, 1H, H_3), 3.30 (br d, J = 12 Hz, 1H, H_1), remaining spectrum obscure. **Minor isomer B** ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.30 (dd, J = 11.0, 2 Hz, 1H, H_3), 3.92 (d, 1H, H_1). **Minor isomer A:** ^{13}C NMR ($CDCl_3$ 125 MHz) δ 125.4, 81.4, 78.5. **Minor isomer B:** ^{13}C NMR δ 123.2, 80.6, 76.4. Other resonances are in the 35−19 range but cannot be assigned.

Di-μ-chloro-dichlorobis(η^3-2-*tert*-butylclododecenyl)dipalladium(II) (51a and 51c, and Di-μ-chlorobis(*exo*-η^3-2-methylene-3,3-dimethylcyclotridecenyl)dipalladium(II) (51b) [PdCl($C_{16}H_{29}$)]$_2$. Reaction of *tert*-butylclododecene according to procedure **A** yielded a yellow solid (1.52 g, 67.6%) composed of **51a** (~80%) and two minor isomers **51b** and **51c**. Anal. Calcd for $C_{32}H_{58}Pd_2Cl_2$: C, 52.96; H, 8.05%. Found: C, 51.72; H, 8.12. *Anti*−*anti* **51a:** ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.66 (dd, J = 10.6, 5.8 Hz, 2H, $H_{1,3}$), 1.09 (s, 9H, *tert*-Bu); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 126.6, 78.2, 35.8, 31.1, 30.6, 27.7, 25.4, 23.3, 21.0. *Syn*−*anti* **51c:** ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.30 (m, 1H, H_1), 3.86 (m, 1H, H_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 129.0, 78.2, 75.5, 35.3, 30.4. **51b:** ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.50 (m, 1H, H_1), 3.90 (s, 1H, H_b), 2.98 (s, 1H, H_a), 1.29 (s, 3H, Me), 1.12 (s, 3H, Me): ^{13}C NMR ($CDCl_3$, 125 MHz) δ 132.5, 78.1, 56.6, 43.1, 38.0, 30.4, 29.3, 26.7, 26.6, 24.9, 23.2, 20.0. ^{1}H Resonances in common: δ 1.90 (m, 4H), 1.75 (m, 2H), 1.30 (m, 32H).

Di-μ-chloro(*exo*-η^3-carophyllenyl)dipalladium(II) [PdCl($C_{15}H_{23}$)]$_2$ (53a). Reaction of β-caryophyllene according to procedure **A** for 1 h at 85 °C yielded a yellow solid (2.42 g, 69.0%) of **53a**. Anal. Calcd for $C_{30}H_{46}Pd_2Cl_2$: C, 52.19; H, 6.72. Found: C, 53.12; H, 6.81. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 4.83 (s, 1H, =CH_2), 4.55 (s, 1H, =CH_2), 4.32 (dd, J = 11.8, 3.8 Hz, 1H, H_2), 3.69 (s, 1H, H_a), 2.94 (s, 1H, H_b), 2.5−1.3 (m, 12H, $H_{3,4,7,8,9, \text{ and } 11}$), 0.94 (s, 3H, Me), 0.92 (s, 3H, Me). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 150.7, 124.7, 113.6, 79.5, 59.9, 49.3, 47.2, 39.4, 38.4, 34.7, 33.2, 31.5, 30.7, 29.9, 21.4.

Di-μ-chlorobis(η^3-2-methylpropenyl)dipalladium(II) [PdCl(C_4H_7)]$_2$ (12). Reaction of 2-methyl-3-chloropropene according to procedure **B** yielded **12** as a yellow solid (1.23 g, 72.4%). Anal. Calcd for $C_8H_{14}Pd_2Cl_2$: C, 24.39; H, 3.58. Found: C, 24.52; H, 3.51. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 3.82 (s, 2H, H_{syn}), 2.85 (s, 2H, H_{anti}), 2.12 (s, 3H, Me). ^{13}C NMR (CD_2Cl_2, 50 MHz): δ 127.5, 62.0, 22.9.

Di-μ-chlorobis(η^3-butenyl)dipalladium(II) [PdCl(C_4H_7)]$_2$ (55). Reaction of 3-chlorobutene according to procedure **B** yielded **55** as a yellow solid (1.15 g, 89.1%). Anal. Calcd for $C_8H_{14}Pd_2Cl_2$: C, 24.39; H, 3.58. Found: C, 24.47; H 3.54. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 5.30 (bd t, J = 11.45, 6.85 Hz, 1H, H_2), 3.88 (dd, J = 11.25, 6.12 Hz, 1H, H_{syn}), 3.83 (d, J = 6.68 Hz, 1H, H_{syn}), 2.77 (d, J = 1.88 Hz, 1H, H_{anti}), 1.30 (d, J = 6.32 Hz, 3H, Me). ^{13}C NMR (CD_2Cl_2, 50 MHz): δ 111.6, 181.8, 59.3, 18.2.

X-ray Determination of (8). Unit-cell parameters were obtained by least-squares analysis on the setting angles for 25 reflections with 44.13° < 2θ < 52.28° using a Rigaku AFC6R diffractometer with graphite-monochromated Mo Kα radiation and a rotating anode generator. A unique data set was measured at 193 ± 1 K within the $2\theta_{max}$ = 60° limit using the ω−2θ scan technique. The intensities of 2915 reflections were collected, with intensities of 3 standard reflections, measured every 150 reflections throughout the data collection, showing only small random variations. Equivalent reflections were merged to yield a unique data set of 2638 reflections. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods[37] and expanded using Fourier techniques. The initial structural refinement assumed that the bridging atoms were chlorides of unit occupancy, however, the displacement factors for chloride refined to atypically low values. When the population parameter for chloride was allowed to refine above unity, the *R* factor lowered significantly.

The increased electron density at the chloride sites was probed with two models. The first assumed disorder within the entire dimer through a 90° rotation, placing Pd and Cl on superimposed sites, which seemed feasible due to the similar Pd−Pd and Cl−Cl distances. Refinement of this model did not find evidence for carbon atoms in the second orientation and was subsequently rejected. The second model assumed contamination of the sample with bromide, and this model was refined by assuming chloride occupancy of p and bromide occupancy of (1 − p), with x, y, z and individual U_{ij}'s constrained to be equal. This single-site model refined well and has been retained.

The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 2404 observed reflections ($I > 1.0\sigma(I)$) and 145 variable parameters and converged to yield unweighted and weighted factors of 0.028 and 0.031, respectively. The weighting scheme was $w = 1/\sigma^2(F_o) = [\sigma_c^2(F_o) + p^2/4(F_o^2]^{-1}$. Neutral scattering

(37) Altomare, A.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.

factors were taken from Cromer and Waber.[38] Anomalous dispersion effects were included in F_{calc},[39] with the values of $\Delta f'$ and $\Delta f''$ taken from Creagh.[40]

X-ray Determination of 7: Unit-cell parameters were obtained by least-squares analysis on the setting angles for 25 reflections with $39.60° < 2\theta < 46.70°$ using a Philips PW1100/20 diffractometer with graphite-monochromated Mo Kα radiation. A unique data set was measured at 293 ± 1 K within the $2\theta_{max} = 55.1°$ limit using the $\omega-2\theta$ scan technique. The intensities of 4155 reflections were collected, of which 4041 were unique with $R_{int} = 0.022$. Intensities of 3 standard reflections, measured every 180 min throughout the data collection, showed only small random variations. No decay correction was required. Indexed crystal faces were used to apply a Gaussian absorption correction, which resulted in transmission factors ranging from 0.533 to 0.878. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods[37] and expanded using Fourier techniques. Initially, all non-hydrogen atoms were refined with anisotropic displacement factors. However, it was noticed that several carbon atoms were very anisotropic, suggesting that these atoms were disordered, corresponding to alternative conformations in the rings. Consequently, C(5), C(6), C(12), and C(13) were each split over two sites, and their relative occupancies were refined while isotropic displacement factors were constrained to be equal. Restraints were placed on C−C distances for these positions, and hydrogen atoms were included at calculated positions. The final cycle of full-matrix least-squares refinement was based on 2712 observed reflections ($I > 1.0\sigma(I)$) and 175 variable parameters and converged to yield unweighted and weighted factors of 0.040 and 0.038, respectively. The weighting scheme was $w = 1/\sigma^2(F_o) = [\sigma_c^2(F_o) + p^2/4(F_o^2]^{-1}$. Neutral scattering factors were taken from Cromer and Waber.[38] Anomalous dispersion effects were included in F_{calc},[39] with the values of $\Delta f'$ and $\Delta f''$ taken from Creagh.[40]

Supporting Information Available: Text giving details of the X-ray study, tables of crystal data and data collection and refinement parameters, positional and thermal parameters, bond distances and angles, torsion angles, and least-squares planes, and figures giving additional views of **7** and **8** (54 pages). Ordering information is given on any current masthead page.

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