direction does not lie in a nodal plane of the $3d_{x^2-y^2}$ orbital. SCF X_α calculations have been successful in assigning the edge transitions for single crystals of $MoO_2S_2^{2-}$.[9,21] We are in the process of extending such calculations to the blue copper site of plastocyanin.

Conclusions

Measurements of the X-ray absorption spectra of plastocyanin crystals in two orientations have enabled us to demonstrate the lack of any EXAFS oscillations attributable to the S(Met) ligand at 2.9 Å from the copper atom and to discover orientation-dependent X-ray absorption edge effects. A possible explanation of the absence of EXAFS oscillations caused by the S(Met) atom is that the motions of the copper and the S(Met) are essentially uncorrelated. Uncorrelated motions, if substantiated, may be taken as an operational definition of nonbonding in cases where crystallographically determined interatomic distances do not lead to an unequivocal description. EXAFS investigation of model compounds with long copper–sulfur bonds could help to determine the generality of this observation. The dichroic absorption edges suggest a location for the Cu $3d_{x^2-y^2}$ orbital that is consistent with a recent redetermination of the electronic structure of the blue copper site.[6]

The failure of EXAFS measurements to detect the presence of an important ligand atom is significant as it demonstrates the risks of using EXAFS as a tool for investigating metal sites in metalloproteins ab initio. However, the present work demonstrates that EXAFS in combination with crystal structure analysis may reveal new details of the bonding in metal coordination environments. Single-crystal EXAFS in particular is shown to provide significant structural information beyond that normally obtained in solution EXAFS experiments.

Acknowledgment. This work was supported by grants from the National Science Foundation (PCM 79-04915), the Australian Research Grants Committee (C 80-15377), and Esso Australia Ltd. and a University of Sydney Research Travel Grant. J.E.H. is the recipient of a National Science Foundation Predoctoral Fellowship, and R.A.S. was supported by a National Institutes of Health Postdoctoral Fellowship (5 F32 HL06047). Synchrotron radiation beam time and some of the equipment and resources used in this study were provided by the Stanford Synchrotron Radiation Laboratory with the financial support of the National Science Foundation (under Contract DMR 77-27489) in cooperation with the Department of Energy and by the National Institutes of Health SSRL Biotechnology Resource (RR 01749). The assistance of Dr. M. Murata and V. A. Norris in the preparation of the plastocyanin specimens is gratefully acknowledged.

Registry No. Plastocyanin, 9014-09-9.

Supplementary Material Available: Tables representing the averaged X-ray absorption data recorded from crystal 2 and crystal 7 in the *b* parallel to the polarization and *c* parallel to the polarization orientations have been deposited as Table II (9 pages). Ordering information is given on any current masthead page.

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Chloropalladation of Alkyl-Substituted Methylenecyclopropanes

Thomas A. Albright,*[1a,d] Paula R. Clemens,[1b] Russell P. Hughes,*[1b,c] Donald E. Hunton,[1b] and Lawrence D. Margerum[1b]

Contribution from the Departments of Chemistry, University of Houston, Houston, Texas 77004, and Dartmouth College, Hanover, New Hampshire 03755. *Received November 23, 1981*

Abstract: The chloropalladation reactions of methylenecyclopropanes bearing alkyl substituents at the three-membered ring are shown to involve 1,3 addition of the elements of Pd–Cl to the organic molecule, with cleavage of the 2,3 σ bond of the ring. Isopropylidenecyclopropane is inert toward chloropalladation, in contrast to 2,2-dimethylmethylenecyclopropane, which gives a 9:1 mixture of **13** and **14**. The cis and trans isomers of 2,3-dimethylmethylenecyclopropane give an identical chloropalladation product, **16**, which exists as a mixture of two diastereoisomeric pairs of enantiomers in a solvent-dependent ratio. The apparent lack of selectivity in the latter reaction is shown to be due to rapid η^3 to η^1 to η^3 transformations of the organic ligand after the chloropalladation step. The true stereochemistry of 1,3 chloropalladation is revealed in the reactions of *cis*-9-methylenebicyclo[6.1.0]nonane (**19**) to give only **20** and of *trans*-9-methylenebicyclo[6.1.0]nonane (**21**) to give a 4:1 mixture of **22** and **23**. Formation of these products is rationalized in terms of suprafacial addition of the elements of Pd–Cl to a ring that is opening stereospecifically in a disrotatory mode, with the breaking bond bending away from the metal. *cis*-7-Methylenebicyclo[4.1.0]heptane (**17**) affords **18** in a reaction that involves suprafacial addition of Pd–Cl while the ring opens disrotatorily with the breaking bond bending toward the metal, followed by a rapid η^3 to η^1 to η^3 isomerization of the kinetic product **25**. The absence of η^3 to η^1 to η^3 interconversions of **20**, **22**, and **23** is rationalized in terms of steric blocking by the nine-membered rings; no such impediment exists for **18**. Monomeric acetylacetonato (acac) derivatives of **16**, **18**, **20**, and **22** are described. Theoretical calculations at the extended Hückel level indicate that the two disrotatory modes of ring cleavage require similar activation energies for a model methylenecyclopropane–$PdCl_2$(NCH) complex. The disrotatory motion of the carbon–carbon bond breaking away from the metal is very slightly favored on electronic grounds. On the other hand, the conrotatory route has a much higher activation energy associated with it. The reaction is, technically, symmetry allowed. The HOMO–LUMO crossing is only weakly avoided, and a small HOMO–LUMO gap is obtained at the transition state. Therefore, the conrotatory path exhibits behavior akin to that in symmetry-forbidden reactions. At some stage in the ring opening, the Cl transfer from Pd to the organic ligand begins. There is a strong interaction between the filled Cl lone-pair orbital and the LUMO of the complex that is concentrated on the two noncoordinated methylene carbons. The Cl transfer should require little, if any, additional activation energy.

The organometallic chemistry of highly strained organic rings has been a topic of considerable interest over the past decade, particularly with regard to the role of transition-metal compounds in the cleavage of carbon–carbon bonds. The transition-metal

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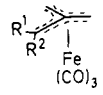
chemistry of methylenecyclopropane and its substituted derivatives has proved to be especially interesting, and several new and useful transformations have been uncovered. Methylenecyclopropanes undergo a variety of catalyzed oligomerization and co-oligomerization reactions, in which the integrity of the three-membered ring can either be maintained or in which ring cleavage can occur;[2] it has been proposed that such oligomerizations proceed via metallacyclic intermediates,[2a-c] and it has been suggested that Ni(0)[2h] and Pd(0)[2a-c] promoted reactions in which ring cleavage occurs may involve oxidative insertion of the metal into the cyclopropane ring to give metallacyclobutane species. These may, in turn, be in equilibrium with metal–trimethylenemethane intermediates.

In stoichiometric organometallic reactions, a number of compounds of Fe(0),[3-5] Rh(I),[3] Ir(I),[3] Pt(II),[3] and Pt(0)[3] have been described that contain methylenecyclopropane derivatives bound to the metal by a simple η^2-olefin linkage. The molecular structures of $[Rh(acac)(\eta^2\text{-methylenecyclopropane})_2]$[3], $[Fe(CO)_4(\eta^2\text{-2,2-diphenylmethylenecyclopropane})]$,[4] and $[Fe(CO)_4\{\eta^2\text{-}endo\text{-}cis\text{-2,3-bis(methoxycarbonyl)methylenecyclopropane}\}]$[5b] have been determined. Stoichiometric ring-opening reactions have also been described. 2,2-Diphenylmethylenecyclopropane has been shown to react with $Fe_2(CO)_9$ to afford a trimethylenemethane–iron complex (**1a**) via cleavage of the 2,3



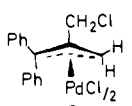
1a $R^1 = R^2 = Ph$
1b $R^1 = Ph; R^2 = H$

σ bond of the cyclopropane ring.[4,6] A similar reaction of 2-phenylmethylenecyclopropane yielded **1b**[4,6,7] as one of the products. Use of selectively deuterium-labeled 2-phenylmethylenecyclopropane has allowed the stereochemistry of ring opening to be defined as disrotatory, with the breaking bond bending away from the metal (dis-out).[4,7a] A theoretical treatment of this reaction has predicted the relative ordering of energies for ring opening in an $[Fe(CO)_3(\eta^2\text{-methylenecyclopropane})]$ intermediate in which the $Fe(CO)_3$ group was taken as pyramidal to be conrotatory < disrotatory out < disrotatory in; notably, both disrotatory modes are formally forbidden by orbital symmetry considerations.[7b] Similarly, apparent dis-out openings of methylenecyclopropane and the cis and trans isomers of 2,3-dimethylmethylenecyclopropane have been reported in their reactions with $Mo(CO)_3(\eta\text{-}C_5Me_5)^+$ to yield cationic η^4-trimethylenemethane compounds.[8]

A number of Fe(0)-promoted reactions of 2-phenylmethylenecyclopropane[4] and the cis and trans isomers of 2,3-bis(methoxycarbonyl)methylenecyclopropane[5] have been shown to afford η-1,3-diene complexes of iron, via cleavage of the 1,2 σ bond of the cyclopropane ring, and the mechanism of this reaction has been the subject of recent discussion.[4] Finally, η-1,4-diene and η-1,3-diene compounds of Fe(0) have been obtained from $Fe_2(CO)_9$-promoted reactions of 2,3-bis(hydroxymethyl)-methylenecyclopropanes.[9]

These reactions involve simple ring opening of the coordinated methylenecyclopropane molecule to yield, in most cases, an organic ligand that is isomeric with the original organic substrate. A variety of stoichiometric ring-opening reactions result in the addition of a ligand, originally in the coordination sphere of the metal, to the coordinated methylenecyclopropane to yield substituted but-3-enyl or allyl complexes. The chloropalladations of the cis and trans isomers of 2,3-bis(methoxycarbonyl)methylenecyclopropane have been studied in detail and proceed via the mechanism shown in Scheme I, using the trans isomer as an example.[10] Compounds **2**, **3**, and **4** were isolated and characterized. The chloropalladation of unsubstituted methylenecyclopropane[11] clearly proceeds via the same mechanism. Hydridoplatination reactions have also been studied; addition of the Pt–H bond of *trans*-$PtH(NO_3)L_2$ (L = tertiary phosphine) to methylenecyclopropane apparently can occur in two ways depending upon the nature of L, as shown in Scheme II.[12] When L is PEt_3, only path a is followed, and addition of Pt–H to the olefin occurs regiospecifically to give only **5**, which can then rearrange to **6** by a series of steps completely analogous to those outlined in Scheme I for chloropalladation. When L is PPh_3, however, a second pathway, b, competes with path a, with addition of Pt–H to the olefin with the opposite regiochemistry to give the coordinatively unsaturated cyclopropylplatinum species **7**, followed by ring opening to produce **8**.[12] Other studies have demonstrated that the ring opening of a coordinatively unsaturated cyclopropyl–Pt to an η-allyl–Pt system is indeed a facile process.[13] The reaction pathways outlined in Scheme II were further substantiated by the isolation of stabilized but-3-enyl- and cyclopropyl–Pt compounds from the hydridoplatination reactions of *cis*- and *trans*-2,3-bis(methoxycarbonyl)methylenecyclopropanes.[14]

We were intrigued by a report that 2,2-diphenylmethylenecyclopropane underwent chloropalladation to give exclusively compound **9**,[11] which clearly must result from cleavage of the 2,3



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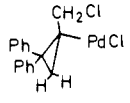

10

σ bond of the ring; this single result stood in contrast to all previous results obtained in the chloropalladations of methylenecyclopropanes.[10] We felt it necessary to contemplate three possible reaction pathways on the basis of previous precedents. First, addition of Pd–Cl to the coordinated olefin could occur in the opposite sense to that observed in other chloropalladations, generating a cyclopropyl–Pd intermediate **10** that could collapse to **9** in a manner analogous to the hydridoplatination path b (Scheme II).[12,14] Second, the possibility of a Pd-promoted ring opening, analogous to that observed with $Fe_2(CO)_9$ (vide supra) and

(1) (a) University of Houston. (b) Dartmouth College. (c) Alfred P. Sloan Research Fellow, 1980–1984. (d) Camille and Henry Dreyfus Teacher–Scholar, 1979–1984.

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(9) (a) Chisnall, B. M.; Green, M.; Hughes, R. P.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1976**, 1899–1907. (b) Green, M.; Hughes, R. P. *Ibid.* **1976**, 1907–1914.

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(11) Noyori, R.; Takaya, H. *J. Chem. Soc. D* **1969**, 525.

(12) Phillips, R. L.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1978**, 1736–1739.

(13) Phillips, R. L.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1978**, 1732–1735.

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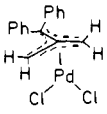
preceding Cl transfer, would generate a trimethylenemethane intermediate **11**;[15] selective migration of Cl to an unsubstituted



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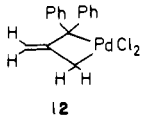


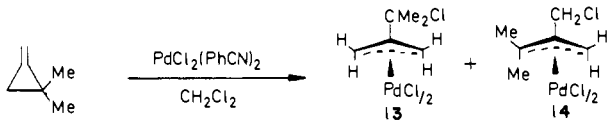
12

terminus would give **9**. Finally, oxidative insertion of "$PdCl_2$" into the cyclopropane ring to afford the metallacycle **12**, followed by selective reductive elimination of C–Cl to give **9**, also had to be considered; analogous insertion reactions of $PtCl_2$ with cyclopropanes are well-known,[17] and the insertion of Pd(0) into the methylenecyclopropane skeletal bonds has also been proposed[2a] (vide supra). Notably, intermediates **11** and **12** could also be interconvertible during the course of the reaction.[2a,h]

We have elucidated the regiochemistry and stereochemistry of this unusual reaction using alkyl-substituted methylenecyclopropanes and have also provided a theoretical description of the ring-opening process using molecular orbital calculations at the extended Hückel level. Some of the results presented here have been the subject of preliminary communications.[18]

Results

The reaction of $PdCl_2(PhCN)_2$ with an equimolar amount of 2,2-dimethylmethylenecyclopropane in CH_2Cl_2, C_6H_6, or MeOH solution proceeded almost instantaneously at room temperature, as evidenced by a color change from deep orange to pale yellow, to afford a virtually quantitative yield of a 9:1 mixture of **13** and **14**. Pure **13** could be isolated by recrystallizing the mixture and



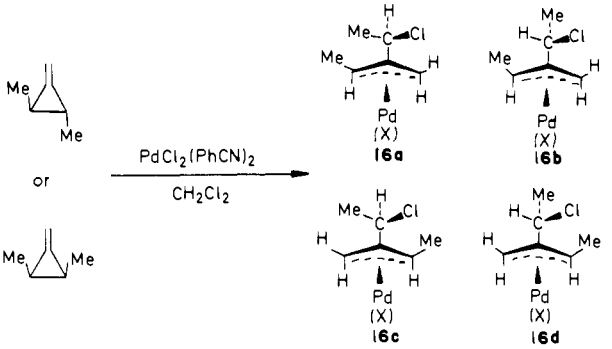
13 + **14**

was found not to convert to **14** in either refluxing benzene or acetonitrile solution.[19] The structures of **13** and **14** were established by their ^1H NMR spectra (Table I). The spectrum of **13** consisted of three singlet resonances, corresponding to the syn, anti, and Me protons, whereas the spectrum of **14** showed two inequivalent Me resonances due to the syn and anti Me groups, two singlet resonances due to the syn and anti protons, and an AB quartet due to the diastereotopic protons of the CH_2Cl group.[21] In contrast, isopropylidenecyclopropane (**15**) showed no tendency

15

to undergo chloropalladation and was unchanged after refluxing with $PdCl_2(PhCN)_2$ in benzene for 8 h.

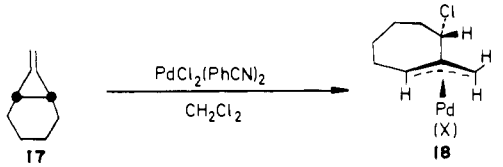
The isomeric compounds *trans*- and *cis*-2,3-dimethylmethylenecyclopropane also underwent rapid chloropalladation (CH_2Cl_2 or C_6H_6; 20 °C) to produce a quantitative yield of a mixture whose 270-MHz ^1H NMR spectrum showed it to be composed of the diastereoisomeric pairs of enantiomers **16a,d** (X = Cl; dimer) and **16b,c** (X = Cl; dimer), with one pair present in a 4:1 excess over the other ($CDCl_3$ solution). In C_6D_6 solution the ratio was 3:1. Duplication of the resonances in this spectrum is unlikely to be due to the presence of syn and anti isomers in solution, since these are only very slight chemical shift differences



16a **16b** **16c** **16d**

between the two sets of resonances (Table I).[22] Treatment of this mixture with Tl(acac) afforded the corresponding mixture of acetylacetonato complexes **16** (X = acac) in which the ratio of diastereoisomeric pairs of enantiomers was found to be 3:1 ($CDCl_3$). The chloropalladation of both *trans*- and *cis*-2,3-dimethylmethylenecyclopropanes was carried out at −60 °C in $CDCl_3$ solution in an attempt to observe the kinetic product(s), but each isomer gave only the same mixture of compounds **16** (X = Cl) in the same ratio under these conditions. Similarly, chloropalladation of these methylenecyclopropanes in MeOH, by using either $PdCl_2(PhCN)_2$ or $PdCl_4^{2-}$, gave an identical mixture of products in almost quantitative yield.[24]

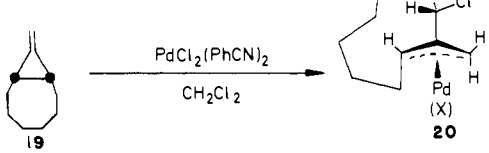
The chloropalladation of *cis*-7-methylenebicyclo[4.1.0]heptane (**17**) [$PdCl_2(PhCN)_2$; CH_2Cl_2 or C_6H_6; 20°] afforded a quanti-



17 **18**

tative yield of a single product **18** (X = Cl^-; dimer) plus its enantiomer. The lack of duplication of ^1H NMR resonances indicated the absence of two diastereoisomeric pairs of enantiomers in this case. Compound **18** (X = Cl) was converted readily into the monomeric complex **18** (X = acac) by treatment with Tl(acac); the ^1H NMR spectrum of **18** (X = acac) exhibited an upfield shift of the protons on carbon atoms directly bound to the metal, compared to their shifts in **18** (X = Cl), thus allowing ready identification of these resonances. An X-ray crystallographic determination of the structure of **18** (X = acac) has shown it to have the configuration depicted in the drawing, with the Cl and Pd on opposite faces of the organic ligand.[25] The tiny ^1H NMR chemical shift change of the C*H*Cl proton in **18** as X was changed from Cl to acac demonstrated that no configurational change occurred during this chemical transformation and that the X-ray structure of **18** (X = acac) reflected the true structure of the chloropalladation product **18** (X = Cl).

Likewise, chloropalladation [$PdCl_2(PhCN)_2$; CH_2Cl_2; 20 °C] of *cis*-9-methylenebicyclo[6.1.0]nonane (**19**) afforded a single



19 **20**

product **20** (X = Cl; dimer) in quantitative yield. Conversion of

(15) The preferred η^3-coordination of d^8 and d^{10} ML_2(trimethylenemethane) species has been the subject of a recent theoretical paper.[16]

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(19) This lack of rearrangement is in contrast to the chloropalladation products of aryl-substituted methylenecyclopropanes.[20]

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(21) The ^1H NMR spectrum of **14** is quite comparable with that reported for **9**.[11,20]

(22) Chemical shift differences of the order of 1 ppm are usually observed for the allylic methine proton in syn and anti isomers.[20,23]

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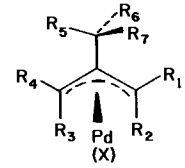
(24) The absence of attack by MeO^- in these systems is contrasted by the ready incorporation of RO^- when the chloropalladation reactions of *cis*- and *trans*-2,3-bis(methoxycarbonyl)methylenecyclopropane are carried out in ROH solution.[10a]

(25) Hughes, R. P.; Day, C. S. *Organometallics* **1982**, *1*, 1221.

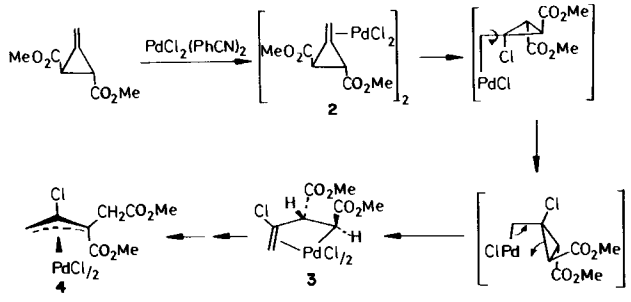
Table I. ^{1}H NMR Data (270 MHz, 30 °C) for Chloropalladation Products[a]



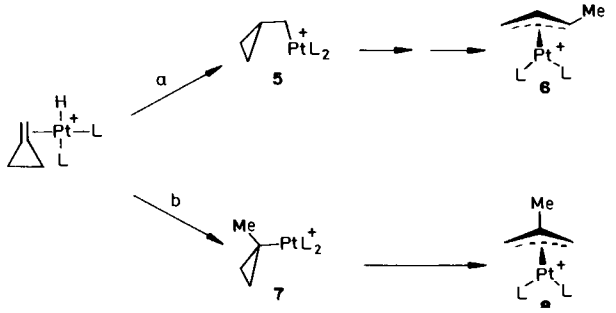
compd	X	R_1	R_3	R_4	R_5	R_6	R_7	R_1	H_2	R_3	R_4	R_5	R_6	R_7	X
13[b]	Cl	H	H	H	Me	Me	Cl	4.18 (s)	2.83 (s)	2.83 (s)	4.18 (s)	1.89 (s)	1.89 (s)		
14[b]	Cl	H	Me	Me	H	H	Cl	3.81 (s)	3.26 (s)	1.32 (s)	1.46 (s)	4.43 (d), J = 12	3.91 (d), J = 12		
16[b,c]	Cl	H	H	Me	Me	H	Cl	3.96 (s)	2.64 (s)	3.76 (q), $J_{3,4}$ = 6.6	1.32 (d), $J_{3,4}$ = 6.6	1.80 (d), $J_{5,6}$ = 6.6	4.88 (q), $J_{5,6}$ = 6.6		
								4.18 (s)	2.57 (s)	3.74 (q) $J_{3,4}$ = 6.6	1.30 (d), $J_{3,4}$ = 6.6	1.70 (d), $J_{5,6}$ = 6.6	4.86 (q), $J_{5,6}$ = 6.6		
16[b,c]	acac	H	H	Me	Me	H	Cl	3.75 (s)	2.46 (s)	3.50 (q), $J_{3,4}$ = 6.6	1.32 (d) $J_{3,4}$ = 6.6	1.79 (d) $J_{3,4}$ = 6.6	4.93 (q), $J_{5,6}$ = 6.6		5.33 (s), CH 1.98 (s), CMe
								3.96 (s)	2.39 (s)	3.47 (q), $J_{3,4}$ = 6.6	1.29 (d), $J_{3,4}$ = 6.6	1.73 (d), $J_{3,4}$ = 6.6	4.92 (q), $J_{5,6}$ = 6.6		1.97 (s), CMe
18[b]	Cl	H	H	$-(CH_2)_4-$	$-(CH_2)_4-$	H	Cl	3.78 (s)	2.83 (s)	3.87 (d, d), $J_{3,4}$ = 6.0, 1.0	1.2–2.5 (m)	1.2–2.5 (m)	4.68 (d, d), $J_{5,6}$ = 5.5, 1.5		
18[b]	acac	H	H	$-(CH_2)_4-$	$-(CH_2)_4-$	H	Cl	3.57 (s)	2.67 (s)	3.57[d]	1.3–2.5 (m)	1.3–2.5 (m)	4.73 (d, d), $J_{5,6}$ = 5.0, 1.5		5.35 (s), CH 2.00 (s), CMe 1.97 (s), CMe
20[b]	Cl	H	$-(CH_2)_6-$	H	H	$-(CH_2)_6-$	Cl	4.36 (s)	3.12 (s)	1.1–2.5 (m)	4.33 (d, d), $J_{3,4}$ = 10, 3	4.22 (d, d), $J_{5,6}$ = 12, 5	1.1–2.5 (m)		
20[e]	Cl	H	$-(CH_2)_6-$	H	H	$-(CH_2)_6-$	Cl	4.36 (s)	2.80 (s)	0.5–2.0 (m)	3.97 (dd), $J_{3,4}$ = 12, 3	3.65 (dd), $J_{5,6}$ = 12, 5	0.5–2.0 (m)		
20[b]	acac	H	$-(CH_2)_6-$	H	H	$-(CH_2)_6-$	Cl	4.14 (s)	2.92 (s)	1.0–2.5 (m)	4.16 (dd), $J_{3,4}$ = 12, 3	4.29 (dd), $J_{5,6}$ = 12, 5	1.0–2.5 (m)		5.35 (s), CH 2.00 (s), CMe 1.98 (s), CMe
22[b]	Cl	H	H	$-(CH_2)_6-$	H	$-(CH_2)_6-$	Cl	4.07 (s)	2.54 (s)	3.72 (dd), $J_{3,4}$ = 11, 6	1.2–2.3 (m)	4.98 (dd), $J_{5,6}$ = 11, 5	1.2–2.3 (m)		
22[b]	acac	H	H	$-(CH_2)_6-$	H	$-(CH_2)_6-$	Cl	3.88 (s)	2.38 (s)	3.47 (dd), $J_{3,4}$ = 11, 5	1.2–2.2 (m)	5.02 (dd), $J_{5,6}$ = 11, 5.5	1.2–2.2 (m)		5.33 (s), CH 1.99 (s), CMe 1.95 (s), CMe
23[b]	Cl	H	$-(CH_2)_6-$	H	Cl	$-(CH_2)_6-$	H	3.84 (s)	3.20 (s)	1.2–2.3 (m)	4.80 (dd), $J_{3,4}$ = 12, 3		1.2–2.3 (m)	4.67 (t), $J_{5,7}$ = 3	

[a] In parts per million downfield from internal Me_4Si (multiplicities: s = singlet, d = doublet, q = quartet, t = triplet, m = multiplet, dd = doublet of doublets), J values are in hertz. [b] $CDCl_3$ solution. [c] Mixture of two diastereoisomeric pairs of enantiomers (see text); the first numbers given correspond to data for the dominant pair. [d] Obscured by H_1 resonance. [e] C_6D_6 solution.

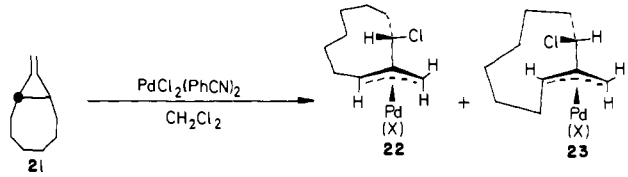
Scheme I



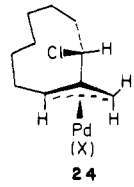
Scheme II



20 (X = Cl) to **20** (X = acac) was effected without any change in the structure of the organic ligand, as evidenced by ^{1}H NMR spectroscopy; once again the protons on carbons directly bonded to Pd appeared at higher field in the acac complex. An X-ray crystallographic determination of the molecular structure of **20** (X = acac) unambiguously established the configuration depicted in the drawing.[18a,25] In contrast, chloropalladation of *trans*-9-methylenebicyclo[6.1.0]nonane (**21**) under identical conditions



afforded a quantitative yield of a 4:1 mixture of two products, neither of which corresponded to **20** (X = Cl). The structures of the major product **22** (X = Cl) and the minor product **23** (X = Cl) were assigned by comparison of ^{1}H NMR shifts with those of **20** (X = Cl), whose configuration was known (vide supra). Notably, the anti proton at the substituted allylic terminus of **22** (X = Cl) resonated at considerably higher field than the corresponding syn proton in **23** (X = Cl).[26] Given that this proton in **23** (X = Cl) is indeed in a syn position, the configuration at the *C*HCl carbon of **23** must be as shown in order that **23** be different from **20** (X = Cl). **24** is an unlikely alternate to structure



22 since the Cl at the *C*HCl carbon atom would undergo a severe interaction with the syn CH_2 group of the nine-membered ring. Recrystallization of the mixture of **22** (X = Cl) and **23** (X = Cl) afforded a sample of pure **22** (X = Cl) which was converted to **22** (X = acac). Unfortunately, suitable crystals for X-ray work proved unattainable for this compound. Finally, the compounds **20**, **22**, and **23** (X = Cl) were all configurationally stable in solution and could be recovered unchanged after 8 h from a refluxing solution of C_6D_6 containing ~5 mol % PPh_3.[27]

Discussion

The structures of the products arising from chloropalladation of the isomeric 9-methylenebicyclo[6.1.0]nonanes **19** and **21** provide the most definitive information concerning the reaction mechanism. Most importantly, it can be assumed that the products **20**, **22**, and **23** (X = Cl) are in each case the kinetic products, since they are isomers that can in theory[28] be interconverted by η^3 to η^1 to η^3 transformations of the allylic–Pd bond in the presence of weak donor ligands. Such ligands, olefin[29] and PhCN, are present in the chloropalladation reaction mixture. Thus, an η^3 to η^1 to η^3 transformation of **20** to **23** (X = Cl), or vice versa, can be achieved by forming the σ bond to Pd from the unsubstituted allylic terminus in the η^1-allyl intermediate. Similarly, the interconversion of **22** and **23** (X = Cl) can be obtained by carrying out an analogous rearrangement and forming the Pd–C σ bond with the substituted end of the allylic ligand.[31] The fact that in practice such isomerizations do not occur, even in the presence of PPh_3 at 80 °C, is remarkable, and it is useful to consider the most plausible reason for this lack of reactivity.

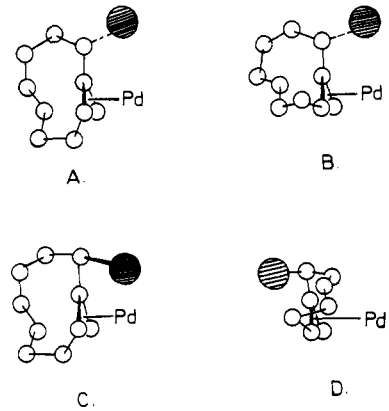


Figure 1. Schematic representations of the ring conformations of the organic ligand in (A) **20**, (B) **22**, (C) **23**, (D) **18**. Open circles, carbon; shaded circles, chlorine.

A crucial feature of isomerization by a η^3 to η^1 to η^3 mechanism is that it requires the transposition of the metal and its attendant ligands from one face of the allyl ligand to the other.[28] Figure 1 illustrates the preferred conformations of the nine-membered rings in **20**, **22**, and **23** and of the seven-membered ring in **18**. The configurations of **18** and **20** are taken directly from the known molecular structures for the acac derivatives of these compounds,[25] while those of **22** and **23** were obtained by using space-filling models (notably, space-filling models of **18** and **20** provide accurate representations of the true structures). In **20**, **22**, and **23** the face of the allyl ligand opposite to the metal is blocked by the rigid $-(CH_2)_6-$ chain, whereas in **18** the $-(CH_2)_4-$ chain winds almost parallel to the three η-allyl carbons and does not sterically block either face. Thus, any η^3 to η^1 to η^3 rearrangement of **20**, **22**, or **23** requires considerable reorganization of the organic ring to accommodate the migrating metal; this factor appears to be sufficient to preclude isomerization. Conversely, isomerization to or from **18** should be more facile and is relevant to subsequent discussion presented below.[32]

Returning to the mechanisms outlined at the end of the introduction, it is possible to exclude them all. Addition of Pd–Cl to the double bond to generate a cyclopropyl–Pd intermediate analogous to **10** cannot be important since Cl clearly migrates to a saturated carbon atom of the original cyclopropane ring. A metallacyclic species analogous to **12** seems most unlikely since such an intermediate cannot be formed from **21** due to the trans-fused bicyclic ring system. Furthermore, the lack of reactivity of **15**, in which the olefin is hindered but the cyclopropane ring is not, clearly points to the former site as being important for interaction with the metal. The mechanism therefore must involve initial coordination of palladium to the double bond followed by ring opening and migration of Cl, i.e., a net 1,3 chloropalladation.

The detailed mechanism of this 1,3 chloropalladation can be deduced from the structures and origins of **20**, **22**, and **23** (X = Cl). Figure 2 depicts the possible chloropalladation pathways for **21**. The possibilities of disrotatory ring opening with the breaking bond bending toward (dis-in) or away (dis-out) from the metal, or conrotatory opening, for which two distinct modes exist, have been considered, as have the options of suprafacial and antarafacial addition of the elements of Pd–Cl. Assuming that ring opening occurs by a single pathway, the experimental observation of two products, **22** (major) and **23** (minor), together with the absence of any **20** rules out the possibility of any conrotatory opening and also precludes antarafacial addition in either the dis-in or dis-out

(26) This difference in chemical shift is a routine method for distinguishing between syn and anti isomers.[20,23]

(27) Such conditions normally induce syn–anti proton site exchange, which is fast on the ^{1}H NMR time scale.[28]

(28) (a) VanLeeuwen, P. W. N. M.; Praat, A. P. *J. Chem. Soc. B* **1970**, 365–366. (b) *J. Organomet. Chem.* **1970**, *21*, 501. (c) *Ibid.* **1970**, *22*, 483–489. (d) VanLeeuwen, P. W. N. M.; Praat, A. P.; Van Diepen, M. *Ibid.* **1970**, *24*, C31–C32. (e) Alexander, C. W.; Jackson, W. R.; Spraat, R. *J. Am. Chem. Soc.* **1970**, *92*, 4990–4992.

(29) Rapid η^3 to η^1 to η^3 transformations of (η-allyl)Pd complexes in solutions containing unsaturated organic molecules are well documented.[30]

(30) (a) Hughes, R. P.; Powell, J. *J. Chem. Soc. D* **1971**, 275–276. (b) *J. Am. Chem. Soc.* **1972**, *94*, 7723–7732. (c) *J. Organomet. Chem.* **1973**, *60*, 387–407. (d) *Ibid.* **1973**, *60*, 409–425.

(31) Formation of the σ bond to the unsubstituted allylic terminus usually is of lower energy.[28]

(32) A similar, though not so severe, blocking effect of a 2-isobutyl or 2-isoamylallyl ligand has been described.[28d]

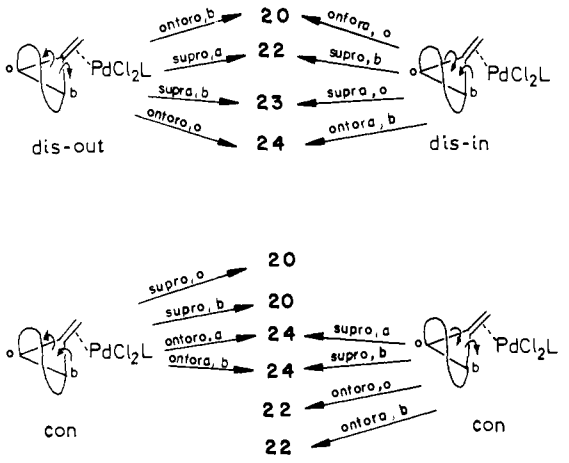


Figure 2. Chloropalladation pathways for **21**.

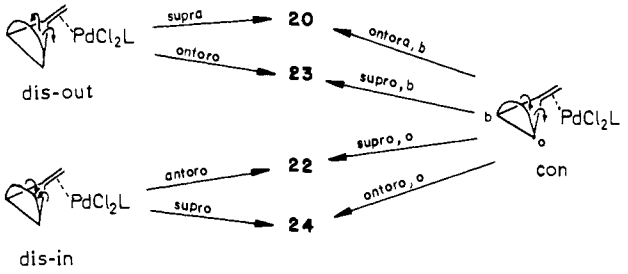
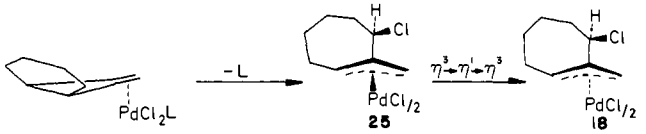


Figure 3. Chloropalladation pathways for **19**.

mode. Of the two possible disrotatory modes, the dis-out mode requires suprafacial migration of Cl to the less hindered C_a in order to produce the major product **22**, while such migration in the dis-in mode requires Cl migration to the more hindered C_b. Clearly this reaction must proceed by dis-out opening of the ring and by suprafacial addition of Pd–Cl. Two important points must be made: First, transfer of Cl from Pd to C must occur very early on in the ring-opening process, since **21** is incapable of opening very far along a dis-out pathway. Second, the dis-in mode may be disfavored due to steric compression of the $-(CH_2)_6-$ chain, and consequently this result does not provide a gauge for the intrinsic electronic preference for dis-in vs. dis-out opening. The first point, however, clearly rules out the intermediacy of a discrete η^4-trimethylenemethane species in this reaction.[33]

Figure 3 depicts the possible chloropalladation pathways for the cis-fused isomer **19**. It has been assumed that coordination of Pd to the olefin will occur preferentially on the less hindered face of the olefin.[34] Once again, dis-in and dis-out modes are possible, together with two equivalent conrotatory openings, one of which is illustrated. Observation of a single product **20** (X = Cl) eliminates all but two possibilities: suprafacial addition of Pd–Cl with dis-out opening, or conrotatory opening and antarafacial addition, with Cl adding selectively to C_b. The demonstrated absence of conrotatory opening and of antarafacial addition of Pd–Cl in the chloropalladation of **21** makes a suprafacial addition with the dis-out opening seem highly probable and creates a consistent, stereoselective mechanism for chloropalladation of both the isomers **19** and **21**. Once again, it should be noted that **19** is incapable of opening very far along a dis-out pathway.

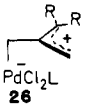
Chloropalladation of *cis*-7-methylenebicyclo[4.1.0]heptane (**17**) also gives a single product **18** (X = Cl), which is structurally related to compound **22** (X = Cl) in terms of the relative configurations at the *C*HCl and substituted allylic carbon atoms. Assuming once again that coordination of Pd should occur to the less hindered face of the olefin,[24] reference to Figure 3 illustrates that formation of **18** directly as the kinetic product from **17** can only occur by antarafacial addition of Pd–Cl during a dis-in opening or by suprafacial addition of Pd–Cl with Cl migrating selectively to C_a during conrotatory opening of the ring. Both pathways are completely inconsistent with the results discussed above. A more plausible explanation is that **18** (X = Cl) is not the kinetic product but that suprafacial addition of Pd–Cl occurs during a dis-in opening. The six-membered ring of **17** would surely be too rigid to permit a dis-out opening.[35] The kinetic product would be **25** (X = Cl), which can convert to **18** (X = Cl) via a



η^3 to η^1 to η^3 rearrangement; there is relatively little steric impediment to this rearrangement (vide supra). That such η^3 to η^1 to η^3 transformations are facile in unhindered systems is evidenced by the observation of a solvent-dependent ratio of diastereoisomeric pairs of enantiomers of **16** (X = Cl); conversion between these diastereoisomeric pairs is completely analogous to conversion of the pair of enantiomers of **25** (X = Cl) with the corresponding pair of enantiomers of **18** (X = Cl). Furthermore, the thermodynamic ratio of diastereoisomeric pairs of **16** (X = Cl) is observed in the chloropalladation of both *cis*- and *trans*-2,3-dimethylmethylenecyclopropane at −60 °C in $CDCl_3$, and η^3 to η^1 to η^3 rearrangement must be facile even at this temperature in the presence of PhCN.

It seems clear, therefore, that in unconstrained systems η^3 to η^1 to η^3 isomerization occurs subsequent to and faster than the actual chloropalladation and precludes observation of the kinetic products. When such isomerization is prevented, the observed stereochemistries of the kinetic products indicate that addition of Pd–Cl occurs suprafacially and that dis-out opening of the ring prevails. When dis-out opening is precluded by ring size, as in **17**, dis-in opening is preferred. No products arising from conrotatory opening are obtained.

We have proposed previously that 1,3 chloropalladation proceeds via a zwitterionic transition state, or intermediate, that might resemble **26**;[18,36] indeed, the regioselectivity of Cl migration in



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the chloropalladation of 2,2-dimethylmethylenecyclopropane supports such an intermediate. However, the clear demonstration that Cl transfer must occur very early in the ring-opening process and the failure to trap any carbonium ion center by carrying out the reactions in a nucleophilic solvent such as methanol indicate that **26** does not intervene as a *discrete intermediate*.

Theoretical Studies

Molecular orbital calculations at the extended Hückel level[37] with computational details given in the Appendix were carried out to probe the ring-opening process. The major object in this portion of the study was not to calculate accurate activation energies and transition states for the ring-opening–chloro-

(33) It has been suggested that palladium(II)–trimethylenemethane species should prefer to adopt an η^3 or η^2 rather than η^4 coordination.[16]

(34) This thermodynamic preference has been established for substitutionally labile d^8 complexes of methylenecyclopropanes[3] and has been assumed by other workers.[4,7a,8]

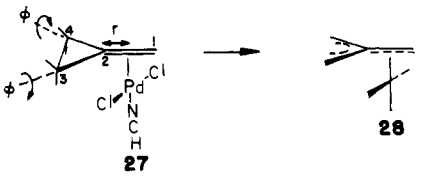
(35) The six-membered ring of **17** is considerably less flexible than the eight-membered ring of **19**. Alternatively, suprafacial addition of Pd–Cl during a dis-out ring opening would generate **25** if the olefin was coordinated to Pd on its more hindered face. Dis-out opening of such a species suffers from precisely the same steric compression as dis-in opening of the isomer in which Pd occupies the less hindered face and there seems to be little driving force to recommend it.

(36) Dallas, B. K.; Hughes, R. P. *J. Organomet. Chem.* **1980**, *184*, C67–C69. See also the discussion in ref 20.

(37) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397–1412. Hoffmann, R.; Lipscomb, W. N. *Ibid.* **1962**, *36*, 2179–2195; **1962**, *37*, 2872–2883. Ammeter, J. H.; Burgi, H. B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686–3692.

palladation sequence. Nor should we try to for a reaction as geometrically complicated as this one at this computational level. Instead, our attention is focused on three issues: why the disrotatory mode of ring opening is preferred over the conrotatory path; what the electronic role of the metal is in the ring opening; and, finally, the outline of the electronic details of the Cl-transfer portion.

It is reasonable to assume that the methylenecyclopropane initially displaces one PhCN ligand in $PdCl_2(PhCN)_2$ to yield a methylenecyclopropane–$PdCl_2(PhCN)$ complex. Several isoelectronic methylenecyclopropane complexes have been isolated.[3] The trans isomer, **27**, has been chosen for convenience. A dis-



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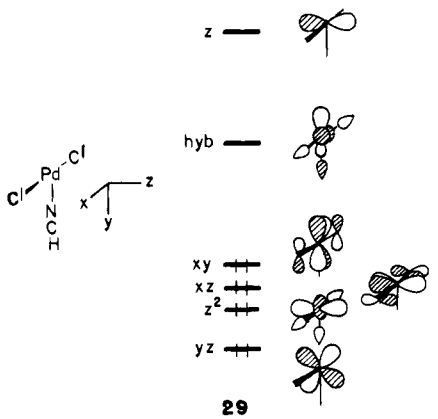
rotatory ring opening to **28** then maintains a mirror plane of symmetry. The more plausible cis isomer would conserve no symmetry element for any of the modes, and unraveling the molecular orbitals is made more difficult. Nonetheless, the primary electronic features are very similar to those that will be outlined below. We have also for computational simplicity replaced the phenyl group on the nitrile ligand by a hydrogen. One of the primary reaction coordinates was chosen to be ϕ (see **27**), the dihedral angle formed between the CH_2 planes and the plane of the cyclopropane ring. In the **27** to **28** conversion, ϕ then varies from 90° to 0°. The C_2–C_3 and C_2–C_4 distances were shortened from 1.48 to 1.41 Å and the C_3–C_2–C_4 angle expanded to 120° in a smoothly continuous fashion along the reaction profile. The distance of the projection of Pd onto the C_1–C_2 axis to C_2, r in **27**, was also independently varied. Furthermore, when the $PdCl_2(HCN)$ unit was moved toward C_2 from the C_1–C_2 midpoint, the Pd–C_2 distance of 2.16 Å was kept constant. When $PdCl_2(HCN)$ was moved away from the midpoint toward C_1, the Pd–C_1 distance was maintained at 2.16 Å. The disrotatory-out, disrotatory-in, and conrotatory pathways (see Figure 2) were studied. The transition states occurred at approximately the same point in the three cases with $\phi = 44°$ and $r = 1.35$ Å. The calculated activation energies for dis-out, dis-in, and con were 13, 18, and 54 kcal/mol, respectively. This is consistent with the experimental results of the previous section—both disrotatory modes are favored over the conrotatory process. The source of this difference is electronic, and the valence orbitals of the methylenecyclopropane and trimethylenemethane isomers are needed to see how this comes about.

The valence orbitals of trimethylenemethane–$PdCl_2(HCN)$ can be constructed from the interaction between the π orbitals of trimethylenemethane and the metal-centered orbitals of a d^8-$PdCl_2(HCN)$ fragment. The latter are simple derivatives of a square-planar system and have been extensively discussed elsewhere.[38] They are shown in **29**. At low energy is a block of



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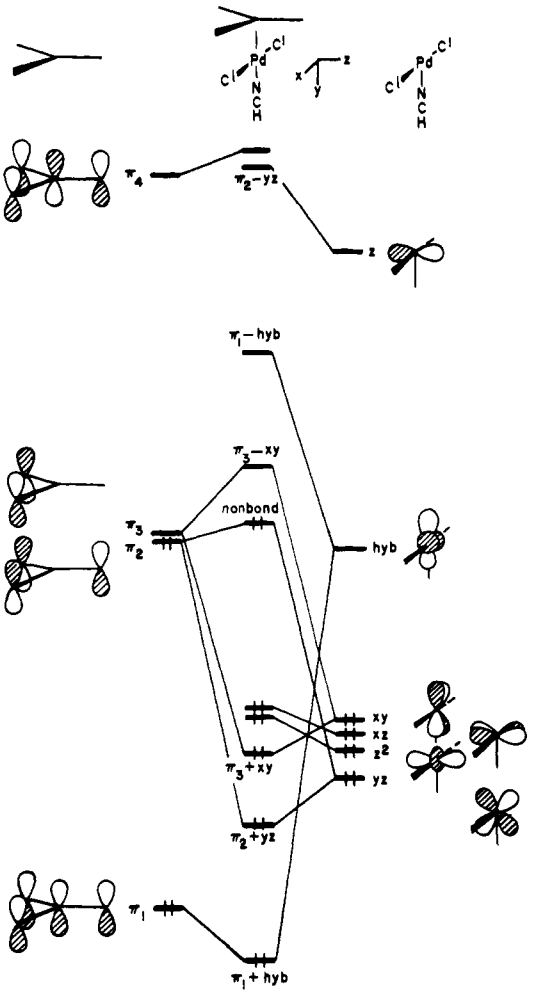
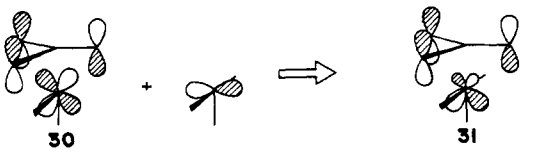


Figure 4. Construction of the valence orbitals of an η^4-trimethylenemethane–$PdCl_2(HCN)$ complex.

four occupied levels. The yz orbital lies lower in energy than the others because it is not destabilized by the Cl lone pairs. Likewise, z^2 lies at somewhat lower energy because of the one empty coordination site. At higher energy is an empty orbital termed "hyb". It is primarily $x^2 - y^2$. Furthermore, metal y and s character are mixed into it. This hybridization is done so that the orbital is directed away from the three ligands toward the empty coordination site. Finally, at high energy is the empty z orbital. Figure 4 shows the construction of the orbitals for an η^4-trimethylenemethane complex. As we shall see, this is not likely to be a viable geometry, but it is instructive to start at this point. The four π orbitals are listed on the left side. π_1 and π_3 form strong bonding and antibonding combinations with hyb and xy, respectively. The bonding orbitals are filled, and antibonding ones are empty. The metal-centered xz and z^2 are essentially nonbonding. Finally, π_2, yz, and z enter into a typical three-orbital pattern. The lowest level, $\pi_2 + yz$, has yz and z mixed into π_2 in a bonding way. $\pi_2 - yz$ is the antibonding counterpart. The middle orbital, nonbond, is π_2 antibonding with respect to yz, **30**. However, what keeps



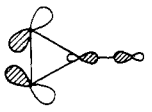
30 **31**

this orbital at low energy is that z mixes into it in a way that is bonding with respect to π_2, yielding **31**. A crucial point in this

(38) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801–3812.

analysis is that nonbond, **31**, lies at a lower energy than $\pi_3 - xy$ (see Figure 4). This is guaranteed for two reasons. Firstly, no matter what degree z mixes into **30**, it will be greater than the amount that metal x can mix into $\pi_3 - xy$. The metal x orbital is destabilized by the two Cl ligands; z is left nonbonding in the $PdCl_2(HCN)$ fragment. Secondly, in the $PdCl_2(HCN)$ fragment, xy must lie at a higher energy, closer to π_2 and π_3 than yz does. As shown in **29**, xy is destabilized by the Cl lone pairs. The symmetry of the fragment precludes this from happening to yz. Since xy must lie closer in energy to the degenerate π_2 and π_3, its antibonding combination will also lie at higher energy. There are some electronic problems with this geometry. Notice that nonbond is a very high-lying *filled* orbital and not far above it is the *empty* $\pi_3 - xy$. The molecule is expected to distort. We shall return to this point.

At this time an orbital correlation can be drawn for the methylenecyclopropane–$PdCl_2(HCN)$ to trimethylenemethane–$PdCl_2(HCN)$ interconversion. This is done in Figure 5 for either of the disrotatory modes that conserve a mirror plane (the yz plane). On the right side are sketched the ten valence orbitals of the trimethylenemethane isomer that were developed in Figure 4. On the left side are displayed the corresponding valence orbitals of the methylenecyclopropane complex. They are the ones expected for a d^8-olefin–ML_3 complex.[38] Also included are the σ and σ^* levels of the C_3–C_4 bond and the empty z orbital at Pd. The orientation of the complex chosen is the one observed for all 16-electron olefin–ML_3 ones[38]—the olefin is oriented perpendicular to the coordination plane. The important point is that this reaction is *symmetry allowed for both disrotatory modes* of ring opening. In actual fact, the σ level is at much higher energy in our calculations (close to the xz, xy orbitals). It is one member of the cyclopropane Walsh set,[39] illustrated by a top view in **32**. It

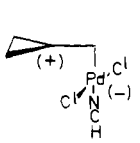


32

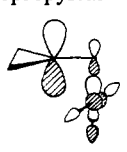
correlates in an enforced sense to the π_1 + hyb or nonbond at the right of Figure 5.

Our calculations suggest that the $PdCl_2(HCN)$ unit does not move toward the central carbon (C_2 in **27**). It rather moves away from it toward C_1 in the ring-opening process. From the "product" side of the reaction, the reason behind this lies in the instability of the η^4 isomer. Moving from η^4 to η^1 stabilizes the nonbond orbital greatly. The mixing of metal z into **30** is shown in a somewhat exaggerated fashion. A good bit of the antibonding between trimethylenemethane and $PdCl_2(HCN)$ is removed in this orbital by the distortion. One might think that this would be counterbalanced by the loss of overlap between xy and π_3. This is actually not the case because the Cl lone pairs are antibonding with respect to xy in $\pi_3 + xy$ and, therefore, also antibonding with respect to the p orbitals on C_3 and C_4. The energy of $\pi_3 + xy$ stays relatively constant along the distortion path. The main driving force is the stabilization of nonbond and to a lesser extent repulsions between Cl lone-pair orbitals and the σ framework of the developing trimethylenemethane ligand so that $PdCl_2(HCN)$ is actually pushed away from the central carbon.

Another way to view this result is to note that slipping from η^2 toward η^1 on the methylenecyclopropane side of the reaction creates a species not unlike the cyclopropylcarbenium ion **33**.



33



34

(39) Jorgenson, W. L.; Salem, L. "The Organic Chemist's Book of Orbitals"; Academic Press: New York, 1973; pp 19–23, 154. It should be noted that the extended Hückel method puts these orbitals at too high an energy.

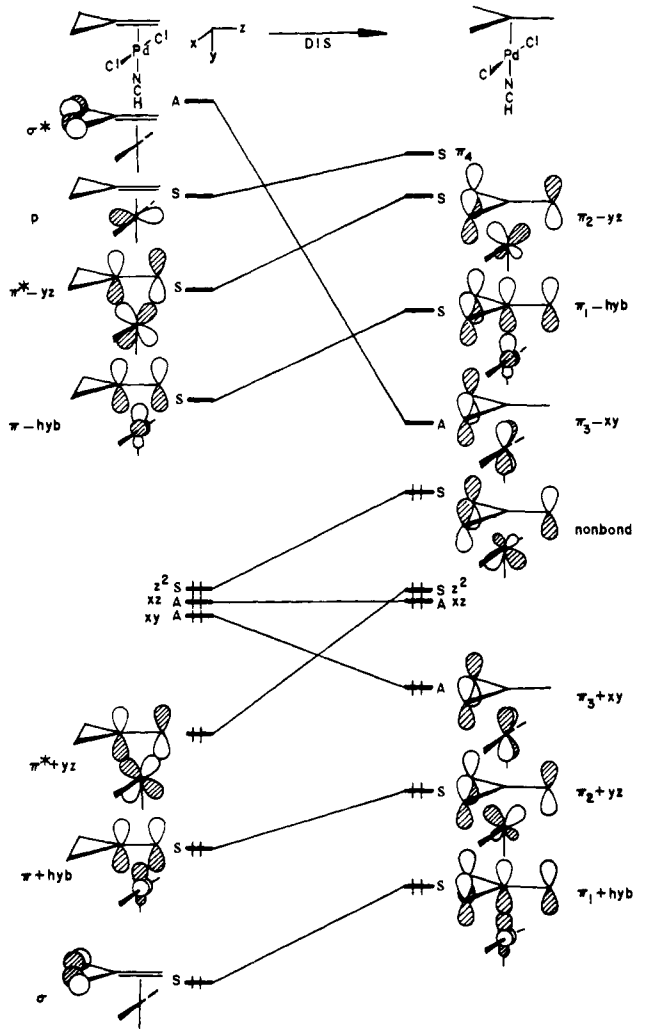


Figure 5. Orbital correlation diagram for either disrotatory mode of the ring-opening reaction. The energy spacing between orbitals has been made more uniform for visual convenience.

Moving $PdCl_2(HCN)$ to r = 1.35 Å creates a charge of +0.349 on C_2. The LUMO, illustrated by **34**, becomes concentrated at C_2. This phenomenon has been treated in detail by Eisenstein and Hoffmann in connection to how the d^8–ML_3 unit activates nucleophilic attack at coordinated olefins.[40] We direct the interested readers to this work for a derivation of the polarization effect in the LUMO. A perhaps oversimplified way to view the ring-opening process is that slipping toward η^1 induces the formation of the cyclopropyl cation that ring-opens in an allowed disrotatory fashion.[41,42]

Figure 6 plots the orbital energies for a section of the potential surface. Here r was fixed at 1.35 Å. The disrotatory-out mode is shown on the left side of this figure. The filled σ level **32** smoothly correlates to nonbond **31**. Likewise, empty σ^* becomes

(40) Eistenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 6148–6149; **1981**, *103*, 4308–4320.

(41) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Verlag-Chemie: Weinheim, 1970; pp 46–7, 55–7.

(42) (a) One can push this analogy still further by utilizing a metallacyclopropane formation that is orbitally equivalent to the olefin–metal one.[38] The $PdCl_2(HCN)$ group is in some sense equivalent to a leaving group. As the slipping motion toward η^1 proceeds, positive charge at C_2 is created, and the C_3–C_4 bond is broken in a disrotatory-out fashion, just as it is in the solvolytic reactions of cyclopropyl halides and related compounds.[41] (b) It should be noted that **33** is *not* an intermediate on the reaction surface. By the time the $PdCl_2(HCN)$ has migrated to r = 1.35 Å, the ring-opening process has gone almost to a half-way mark. Rotation about the C_1–C_2 is also very hindered. There still is a good bit of π bonding that is retained. In fact the C_1–C_2 overlap population stays relatively constant for calculations of **27** r = 0.705 Å, ϕ = 90°; r = 1.35 Å, ϕ = 90°; and r = 1.41 Å, ϕ = 0°.

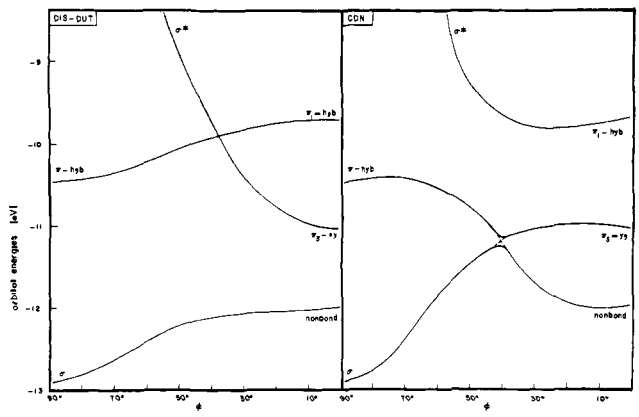


Figure 6. Evolution of the HOMO and two LUMO's as a function of ϕ defined in **27** for r = 1.35 Å. The divisions of the energy scale on the left are in units of electron volts.

$\pi_3 - xy$. In the conrotatory path, there will be an attempted correlation of σ to $\pi_3 - xy$. Considering the methylenecyclopropane ligand itself, this correlation is an exact one. However, the complex does not possess the crucial C_2 symmetry axis that would have been conserved along a conrotatory path, and so σ still technically correlates to nonbond. The right side of Figure 6 shows this. The intended orbital crossing, shown by a dashed line, is only weakly avoided.[43] This means that the HOMO must rise to a very high energy, and the corresponding activation energy becomes much greater (54 kcal/mol) than either of the disrotatory paths (13 and 18 kcal/mol for dis-out and dis-in, respectively). At the transition state for the dis-out and dis-in paths, the HOMO–LUMO gap is calculated to be 2.2 and 2.0 eV, respectively. However, in the conrotatory mode, the energy gap was only 0.1 eV. Thus, the conrotatory path while being technically symmetry allowed has all of the characteristics of a symmetry-forbidden reaction.

The larger activation energy for dis-in compared to dis-out comes from two sources. Firstly, as σ evolves into nonbond, the orbitals at C_3 and C_4 are antibonding with respect to Pd yz. Secondly, antibonding is greater for the dis-in mode to at least ϕ = 45° than for dis-out. There is also a clear steric preference at work. The endo hydrogens on C_3 and C_4 come much closer to the two Cl's in the dis-in pathway. The 5 kcal/mol difference between the dis-in and dis-out represents a maximum value. The methylenecyclopropane ring was taken to be planar. Allowing the C_3, C_4 portion of the ring to bend 15° out of the plane, away from Pd, causes the difference to be 3 kcal/mol. The methylenecyclopropane ligand is, indeed, puckered in this direction in d^8-square-planar complexes.[3]

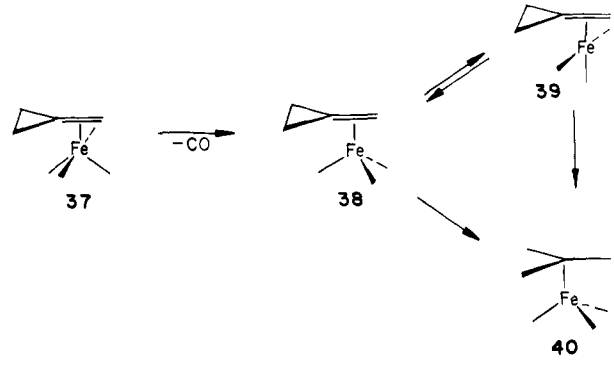
It is easy to see how the Cl-transfer portion of the reaction must proceed. Our experimental studies on chloropalladation of **19** and **21** are consistent only with a suprafacial and, therefore, intramolecular migration of Cl from Pd to either of the noncoordinated methylene carbons. At the end of the ring-opening stage of the reaction, the optimum value of r (defined in **27**) was found to be 1.40 Å. The electronic structure of the trimethylenemethane complex resembles zwitterionic **26**. The C_3, C_4 carbons have a charge of +0.313. The LUMO, **35**, at this geometry is essentially

35 **36**

π_3 with little contribution at the metal. Rotation by 60° about the Pd–C_1 axis brings one of the Cl ligands close to a methylene carbon. The corresponding C–Cl distance becomes 2.16 Å. As rotation proceeds, the LUMO mixes into the two occupied Cl lone-pair orbitals whose radial extent is along the y axis. The mixing occurs in a bonding way, as is shown in **36** for the symmetric member of the lone-pair orbitals. Thus, the C–Cl overlap population grows rapidly upon rotation. At some point the Pd–Cl distance must lengthen, and the resulting PdCl(HCN) unit migrates to the allyl position. The evolution of the orbitals is quite complicated, and we will not reproduce the arguments here. Suffice it to say that there appears to be no significant destabilization of any of the orbitals and, hence, a substantial activation energy is not expected for the Cl-transfer portion of the reaction.

It has been instructive to divide the reaction into separate ring-opening and chloropalladation steps. However, there is no compelling electronic reason for the intermediacy of a discrete η^1-trimethylenemethane species. As pointed out in the last section, our experimental evidence points strongly to the absence of **26** as an intermediate. Thus, we envision the reaction to occur in one step. The timing of the events should be quite sensitive to the geometrical constraints imposed by substituents on the methylenecyclopropane ring. However, the following qualitative generalizations should apply. Movement of the $PdCl_2(HCN)$ unit toward η^1 occurs rapidly according to our calculations. This initiates the C_3–C_4 bond breaking. As ϕ decreases from 90°, positive charge develops at C_3 and C_4. This, in turn, induces rotation of $PdCl_2(HCN)$ and the actual chloropalladation sequence. At what value of ϕ this stage occurs is not crucial to our arguments concerning the mode of ring opening. As shown in Figure 6, the HOMO for the conrotatory path rises much more steeply than either disrotatory paths.

There may be a connection here between our mechanism and the $Fe_2(CO)_9$-induced ring opening of methylenecyclopropanes.[4-7] The initial olefin–$Fe(CO)_4$ complex **37** loses a CO ligand to give



37 **38** **39** **40**

a methylenecyclopropane–$Fe(CO)_3$ intermediate,[44] presumably with a pseudotetrahedral structure, **38**. Pinhas and Carpenter have shown[7] that the disrotatory modes of ring opening to the η^4-trimethylenemethane–$Fe(CO)_3$ complex, **40**, are symmetry forbidden. However, the dis-out path has been experimentally shown to be the favored one for sterically nonbiased systems.[4,7a] One way to bypass the symmetry restriction would be to distort to a square-planar intermediate, **39**. The topology of the valence orbitals in **39** is identical with those shown on the left side of Figure 5, and a disrotatory path is now symmetry allowed. Calculations on ethylene–$Fe(CO)_3$ have been carried out.[45] A full-scale geometrical optimization gave a highly distorted tetrahedral form, analogous to **38** with the olefin rotated by 90°, as a local minimum. However, it is 4 kcal/mol less stable than a square-planar geometry, analogous to **39**. Additionally there is a 4-kcal/mol barrier on going from the "tetrahedral" to square-planar form. We know of no d^8-olefin–$M(CO)_3$ structure to corroborate our prediction. Another related complex is $Fe(CO)_4$, and although there has been much work done on its structure, nothing yet is known about the

(43) For a discussion of avoided crossings, see: Salem, L.; Leforestier, C.; Segal, G.; Wetmore, R. *J. Am. Chem. Soc.* **1975**, *97*, 479–487 and references therein.

(44) A methylenecyclopropane–$Fe(CO)_3$ intermediate is mandated by the induced kinetic deuterium isotope effect observed for this system, see ref 4b.

(45) Albright, T. A., to be published.

geometry of the *singlet* state. The triplet state has a distorted tetrahedral geometry.[46] The ring opening of **39** should initially proceed in a way that is very similar to the $PdCl_2(RCN)$ complex. The dis-out pathway is slightly preferred over dis-in, which in turn is greatly favored over the con pathway. As the $Fe(CO)_3$ group moves toward the central carbon, however, it will pyramidalize. Referring back to the right side of Figure 5, we see that pyramidalization stabilizes nonbond, z^2, and xz. They become a set of three "t_{2g}-like" orbitals.[47] Furthermore, $\pi_3 + xy$ along with $\pi_2 + yz$ become an e set. The metal orbitals are reoriented to provide maximal bonding to trimethylenemethane π_2 and π_3 (see Figure 4).

Conclusions

The stereochemistry of chloropalladation for most methylenecyclopropane derivatives is masked because the kinetic products are converted into thermodynamically more stable ones by rapid η^3 to η^1 to η^3 transformations. The facts that both *cis*- and *trans*-2,3-dimethylmethylenecyclopropane yield the same product ratio of **16** and that this ratio is solvent dependent argues strongly in favor of this proposal. The folding of the $-(CH_2)_6-$ chain in **20**, **22**, and **23** makes these kinetic products configurationally stable. These products demonstrate that dis-out ring cleavage and suprafacial addition of Pd–Cl occur for chloropalladation of *cis*- and *trans*-9-methylenebicyclo[6.1.0]nonane (**19** and **21**). Any of the three modes of ring opening are geometrically possible for especially **19**, and therefore, dis-out should be the path of lowest energy for unconstrained systems as well. The molecular orbital calculations in the parent system are also in agreement with this. The two disrotatory modes should be close in energy. Our experimental data show that the dis-in process is also feasible in *cis*-7-methylenebicyclo[4.1.0]heptane, **17**, where the dis-out process is geometrically made unfavorable. Most noteworthy is the fact that products from a conrotatory mode with a suprafacial addition are not observed. The con path is predicted to strongly resemble a symmetry-forbidden reaction. A high activation energy is associated with it. Orbital symmetry rules developed for these transition-metal-assisted electrocyclic reactions[7b,16] must take into account not only the number of electrons at the metal but also the number and geometrical position of the other ligands coordinated to the metal.

Experimental Section

General Procedures. All reactions were run under an atmosphere of dry nitrogen. Spectrograde solvents (Fisher) were used without further purification. ^1H NMR spectra were run at 270 MHz at the Northeast NSF Regional NMR Facility at Yale University. Microanalyses were performed by Spang, Ann Arbor, MI.

cis- and *trans*-2,3-dimethylmethylenecyclopropane,[48] 2,2-dimethylmethylenecyclopropane,[48] isopropylidenecyclopropane,[49] *cis*-7-methylenebicyclo[4.1.0]heptane,[48] and *cis*-9-methylenebicyclo[6.1.0]nonane[48] were prepared by literature methods.

***trans*-9-Methylenebicyclo[6.1.0]nonane.** *n*-Butyllithium (Alfa) (37.5 mL of a 2.4 M hexane solution; 0.108 mol) was added dropwise to a solution of *trans*-cyclooctene[50] (11.8 g; 0.108 mol) and 1,1-dichloroethane (10.7 g; 0.108 mol) in diethyl ether (40 mL) over a period of 1 h at −30 °C. The mixture was warmed to 25 °C and stirred overnight. Water (30 mL) was added cautiously, and the organic layer was separated, dried ($MgSO_4$), and filtered. Ether was distilled at atmospheric pressure, and the residue was fractionally distilled to afford *trans*-9-chloro-9-methylbicyclo[6.1.0]nonane: 4.32 g; 0.025 mol; 23%; bp 57–63 °C (0.95 torr); ^1H NMR ($CDCl_3$) δ 1.60 (s, CH_3); 0.5–2.3 (m, CH and CH_2). GC analysis (Varian 3700 Chromatograph, 20-m silicon-fused glass capillary column) demonstrated that the product was 99% pure.[51]

To a solution of *trans*-9-chloro-9-methylbicyclo[6.1.0]nonane (2.01 g, 0.018 mol) in dimethyl sulfoxide (5 mL) was added (dropwise, 0.5 h) a solution of potassium *tert*-butoxide (1.31 g, 0.018 mol) in dimethyl sulfoxide (11 mL) at 25 °C. The resultant yellow solution was poured onto ice (50 g), and the mixture was extracted with isopentane (3 × 25 mL). The isopentane extract was dried ($MgSO_4$) and filtered, and the isopentane was distilled at atmospheric pressure. Fractional distillation of the residue at reduced pressure afforded *trans*-9-methylenebicyclo-[6.1.0]nonane: 0.95 g; 0.0077 mol; 71% yield; 99% pure by GC; ^1H NMR ($CDCl_3$) δ 5.34 s, $=CH_2$; 0.4–2.5 (m, CH and CH_2). *Note*: Inverse addition of the chlorocyclopropane to the solution of base gave a 3:2 mixture of both *trans*- and *cis*-9-methylenebicyclo[6.1.0]nonanes. Clearly, isomerization of the strained trans isomer of the product must occur in the presence of excess *t*-BuO^-.[52]

Chloropalladation of 2,2-Dimethylmethylenecyclopropane. To a solution of $PdCl_2(PhCN)_2$ (0.511 g, 1.33 mmol) in CH_2Cl_2 (50 mL) was added 2,2-dimethylmethylenecyclopropane (0.11 g, 1.34 mmol) at 25 °C. The red-orange solution rapidly turned pale yellow. Evaporation of the solvent under reduced pressure followed by exposing the oily residue to high vacuum (10^{-2} torr) for 6 h left a yellow solid whose ^1H NMR spectrum showed it to be a 9:1 mixture of compounds **13** and **14** (0.340 g, 0.65 mmol, 98%). Recrystallization from CH_2Cl_2/hexane afforded pure **13** (0.250 g), mp 100–105 °C dec. Anal. Calcd for $[C_6H_{10}Cl_2Pd]_2$: C, 27.78; H, 3.88. Found: C, 27.85; H, 4.00. Similar reactions run using C_6H_6 or CH_3OH as solvent gave an identical mixture of products. A solution of **13** (0.100 g) in C_6H_6 (20 mL) was heated under reflux for 4 h; evaporation of the solvent left unchanged **13**, as evidenced by its ^1H NMR spectrum. A similar reflux of **13** in CH_3CN solution resulted in no change.

Attempted Chloropalladation of Isopropylidenecyclopropane. A solution of $PdCl_2(PhCN)_2$ (0.100 g, 0.26 mmol) and isopropylidenecyclopropane (1 mL) in C_6D_6 (5 mL) was heated to reflux for 8 h in the presence of PhCN (0.10 mL). After the solution was cooled to 25 °C, a small amount of insoluble material was filtered off, and the ^1H NMR spectrum of the filtrate showed only resonances attributable to PhCN and isopropylidenecyclopropane.

Chloropalladation of *cis*- and *trans*-2,3-Dimethylmethylenecyclopropanes. To a solution of $PdCl_2(PhCN)_2$ (0.500 g, 1.30 mmol) in CH_2Cl_2 (50 mL) was added *cis*-2,3-dimethylmethylenecyclopropane (0.11 g, 1.34 mmol) at 25 °C. The red-orange solution rapidly turned pale yellow. Evaporation of the solvent under reduced pressure followed by exposure of the residue to high vacuum (10^{-2} torr) for 4 h afforded a yellow solid whose ^1H NMR spectrum ($CDCl_3$) showed it to consist of the diastereoisomeric pairs of enantiomers of **16** (X = Cl) (0.335 g, 0.65 mmol, 99%). Recrystallization of this material from CH_2Cl_2/hexane (−30 °C) yielded an analytical sample of pale yellow needles (mp 120–123 °C dec). Anal. Calcd for $[C_6H_{10}Cl_2Pd]_2$: C, 27.78; H, 3.88. Found: C, 27.90; H, 4.10. Similar reactions run in either C_6H_6 or CH_3OH solutions yielded an identical product.

Alternatively, a solution of Na_2PdCl_4 (0.250 g, 0.85 mmol) in CH_3OH (50 mL) was treated with *cis*-2,3-dimethylmethylenecyclopropane (0.10 g, 1.22 mmol). The red-brown solution quickly became pale yellow. The solution was poured into H_2O (200 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The organic layer was dried ($MgSO_4$) and filtered, and the solvent was removed under reduced pressure to afford a sample of **16** [X = Cl] (0.210 g, 0.41 mmol, 95%) identical in every respect with that obtained by the former procedure.

Alternatively, a solution of $PdCl_2(PhCN)_2$ (0.100 g, 0.26 mmol) in $CDCl_3$ (3 mL) in an NMR tube was cooled to −60 °C in the probe of the NMR spectrometer. *cis*-2,3-Dimethylmethylenecyclopropane (0.025 mL) was added through a septum by using a GC syringe. The tube was quickly removed from the probe, inverted once to mix the contents, and replaced in the probe. A ^1H NMR spectrum was recorded within 1 min of mixing, and at 5-min intervals thereafter. The resonances of the methylenecyclopropane diminished over a period of ca. 0.5 h and were replaced by the resonances of the identical mixture of diastereoisomeric pairs of enantiomers of **16** (X = Cl) obtained in the room-temperature reaction.

(46) (a) Barton, T. J.; Grinter, R.; Thompson, A. J.; Davies, B.; Poliakoff, M. *J. Chem. Soc., Chem. Common.* **1977**, 841 and references therein. (b) There has been little theoretical agreement on the geometry of the singlet form, see: Pensak, D. A.; McKinney, R. J. *Inorg. Chem.* **1979**, *18*, 3407–3413 and references therein.

(47) For the orbitals of C_{3v} trimethylenemethane–$Fe(CO)_3$, see: Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546–7557.

(48) Arora, S.; Binger, P. *Synthesis* **1974**, 801–803.

(49) Utimoto, K.; Tamura, M.; Sisido, K. *Tetrahedron* **1973**, 1169–1171.

(50) Bridges, A.; Whitham, G. *J. Chem. Soc., Chem. Commun.* **1974**, 142–143.

(51) In contrast to the analogous cyclopropane derived from *cis*-cyclooctene,[48] this compound can only exist as one isomer; no syn–anti isomers are possible.

(52) Such an isomerization presumably occurs via the transient cyclopropylcarbanion formed by proton abstraction from the three-membered ring. Experiments using *t*-BuO^- in Me_2SO-d_6 indicate that such cyclopropyl hydrogens are kinetically acidic under these conditions,[20] but it should be noted that the cis and trans isomers of 2,3-dimethylmethylenecyclopropane can be prepared stereochemically pure in the presence of excess *t*-BuO^- in Me_2SO at 60 °C.[48] We attribute the apparent facility of cyclopropyl carbanion inversion in this case to the strain imposed by the trans-fused rings.

Table II. Parameters Used in the Extended Hückel Calculations

orbital	H_{ii}, eV	ζ_1	ζ_2	C_1[a]	C_2[a]
Pd 4d	−12.02	5.983	2.613	0.5535	0.6701
5s	−7.32	2.190			
5p	−3.75	2.152			
Cl 3s	−30.00	2.033			
3p	−15.00	2.033			
C 2s	−21.40	1.625			
2p	−11.40	1.625			
N 2s	−26.00	1.950			
2p	−13.40	1.950			
H 1s	−13.60	1.300			

[a] Contraction coefficients used in the double-ζ expansion.

Utilization of *trans*-2,3-dimethylmethylenecyclopropane in any of the above procedures gave identical results.

Preparation of 16 (X = acac). To a solution of **16** (X = Cl) (0.400 g, 0.77 mmol) in CH_2Cl_2 (20 mL) was added Tl(acac) (0.500 g, 1.65 mmol), and the resultant mixture was stirred for 2 h. Pentane (20 mL) was added, and the mixture was filtered through a Celite plug. The filtrate was evaporated to dryness under reduced pressure and the residue recrystallized from CH_2Cl_2/pentane to afford **16** (X = acac) as white needles (0.405 g, 1.25 mmol, 81%), mp 96–98 °C dec. Anal. Calcd for $C_{11}H_{17}ClO_2Pd$: C, 40.89; H, 5.30. Found: C, 41.02; H, 5.35.

Chloropalladation of *cis*-7-Methylenebicyclo[4.1.0]heptane. A solution of $PdCl_2(PhCN)_2$ (0.520 g; 1.36 mmol) in CH_2Cl_2 (50 mL) was treated with *cis*-7-methylenebicyclo[4.1.0]heptane (0.150 g, 1.39 mmol). The red-orange solution rapidly turned pale yellow. Removal of the solvent under reduced pressure followed by exposure of the residue to high vacuum (10^{-2} torr) for 4 h afforded a yellow solid, shown by its ^1H NMR spectrum to consist entirely of **18** (X = Cl) (0.372 g, 0.65 mmol, 96%). Recrystallization from CH_2Cl_2/hexane (−30 °C) afforded an analytical sample of pale yellow needles, mp 100–103 °C dec. Anal. Calcd for $[C_8H_{12}Cl_2Pd]_2$: C, 33.66; H, 4.24. Found: C, 33.75; H, 4.30. Similar reactions using C_6H_6 or CH_3OH as solvent yielded an identical product. A reaction of $PdCl_2(PhCN)_2$ with *cis*-7-methylenebicyclo[4.1.0]heptane in an NMR tube ($CDCl_3$, −60 °C) as described above likewise yielded only **18** (X = Cl).

Preparation of 18 (X = acac). A solution of **18** (X = Cl) (0.320 g, 0.56 mmol) in CH_2Cl_2 (20 mL) was treated with Tl(acac) (0.350 g, 1.15 mmol), and the mixture was stirred for 2 h. Pentane (20 mL) was added, and the mixture was filtered through a Celite plug. Removal of the solvent from the filtrate under reduced pressure followed by recrystallization of the residue from CH_2Cl_2/pentane (−30 °C) yielded **18** (X = acac) as cream prisms (0.330 g, 0.094 mmol, 84%), mp 94–98 °C dec. Anal. Calcd for $C_{13}H_{19}ClO_2Pd$: C, 44.72; H, 5.48. Found: C, 44.99; H, 5.60.

Chloropalladation of *cis*-9-Methylenebicyclo[6.1.0]nonane. A solution of $PdCl_2(PhCN)_2$ (1.10 g, 2.87 mmol) in CH_2Cl_2 (75 mL) was treated with *cis*-9-methylenebicyclo[6.1.0]nonane (0.400 g, 2.94 mmol). The red-orange solution rapidly turned pale yellow. Removal of the solvent under reduced pressure and exposure of the residue to high vacuum (10^{-2} torr) for 2 h yielded a yellow solid, which was shown by its ^1H NMR spectrum to consist entirely of **20** (X = Cl) (0.890 g, 1.42 mmol, 99%). Recrystallization from CH_2Cl_2/hexanes (−30 °C) afforded an analytical sample, mp 151–154 °C dec. Anal. Calcd for $[C_{10}H_{16}Cl_2Pd]_2$: C, 38.31; H, 5.14. Found: C, 38.50; H, 5.20. A sample of **18** (X = Cl) (0.100 g, 0.16 mmol) and PPh_3 (0.005 g, 0.002 mmol) in C_6D_6 (2 mL) was heated to reflux for 8 h. On cooling, the ^1H NMR spectrum of the sample was unchanged.

Preparation of 20 (X = acac). A solution of **20** (X = Cl) (0.700 g, 1.12 mmol) in CH_2Cl_2 (50 mL) was treated with Tl(acac) (0.700 g, 2.31 mmol), and the mixture was stirred for 2 h. Pentane (50 mL) was added, and the mixture was filtered through a Celite plug. Removal of the solvent from the filtrate under reduced pressure followed by recrystallization of the residue from CH_2Cl_2/pentane yielded **18** (X = acac) as pale yellow prisms (0.750 g, 1.99 mmol, 89%), mp 120–123 °C dec. Anal. Calcd for $C_{15}H_{23}ClO_2Pd$: C, 47.76; H, 6.15. Found: C, 47.80; H, 6.20.

Chloropalladation of *trans*-9-Methylenebicyclo[6.1.0]nonane. A solution of $PdCl_2(PhCN)_2$ (0.600 g, 1.56 mmol) in CH_2Cl_2 (50 mL) was treated with *trans*-9-methylenebicyclo[6.1.0]nonane (0.220 g, 1.62 mmol). The red-orange solution rapidly turned pale yellow. Removal of the solvent under reduced pressure and exposure of the residue to high vacuum (10^{-2} torr) for 4 h yielded a yellow glassy solid, shown by its ^1H NMR spectrum to consist of a 4:1 mixture of **22** and **23** (X = Cl) (0.480 g, 0.76 mmol, 98%). Recrystallization from CH_2Cl_2/hexane (−30 °C) afforded a sample of pure **22** (X = Cl) (0.250 g), mp 133–135 °C dec. Anal. Calcd for $[C_{10}H_{16}Cl_2Pd]_2$: C, 38.31; H, 5.14. Found: C, 38.35; H, 5.18. A 4:1 mixture of **22** and **23** (X = Cl) (0.100 g, 0.16 mmol) and PPh_3 (0.005 g, 0.002 mmol) in C_6D_6 (2 mL) was heated to reflux for 10 h. On cooling, the ^1H NMR spectrum of the sample was unchanged, indicating no interconversion between **22** and **23** (X = Cl) and no formation of **20** (X = Cl).

Preparation of 22 (X = acac). This compound was prepared from **22** (X = Cl) in a manner similar to that described for **20** (X = acac) and was obtained as fine pale yellow needles (82%), mp 109–111 °C dec. Anal. Calcd for $C_{15}H_{23}ClO_2Pd$: C, 47.76; H, 6.15. Found: C, 47.89; H, 6.26.

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Appendix

The parameters used in the extended Hückel calculations[37] are listed in Table II. The H_{ii} values for Pd were taken from other work.[53] All Pd–Cl, Pd–N, C–N, and C–H distances were set at 2.30, 2.03, 1.18, and 1.09 Å, respectively. The Pd–methylenecyclopropane (or trimethylenemethane) distance was varied as described in the text. The C_2–C_3, C_2–C_4, and C_3–C_4 distances were fixed at 1.48 Å for the methylenecyclopropane complex. The C_2–C_3 and C_2–C_4 distances were shortened to 1.41 Å in the trimethylenemethane geometry. The Cl–Pd–N, Pd–N–C, and N–C–H angles were idealized at 90°, 180°, and 180°, respectively.

Registry No. 13, 70417-10-6; **14**, 82740-55-4; **16a** (X = Cl), 82795-55-9; **16b** (X = Cl), 82795-56-0; **16c** (X = Cl), 82795-57-1; **16d** (X = Cl), 82795-58-2; **16a** (X = acac), 82740-56-5; **16b** (X = Acac), 82795-59-3; **16c** (X = acac), 82795-60-6; **16d** (X = acac), 82795-61-7; **18** (X = Cl), 82796-01-8; **18** (X = acac), 82495-27-0; **20** (X = Cl), 77773-11-6; **20** (X = acac), 77773-12-7; **22** (X = Cl), 77842-80-9; **22** (X = acac), 82795-62-8; **23** (X = Cl), 77842-81-0; *trans*-cyclooctene, 931-89-5; *trans*-9-chloro-9-methylbicyclo[6.1.0]nonane, 82795-63-9; *trans*-9-methylenebicyclo[6.1.0]nonane, 77769-30-3; isopropylidenecyclopropane, 4741-86-0; 2,2-dimethylmethylenecyclopropane, 4372-94-5; *cis*-2,3-dimethylmethylenecyclopropane, 5070-00-8; *cis*-7-methylenebicyclo[4.1.0]heptane, 54211-14-2; *cis*-9-methylenebicyclo[6.1.0]nonane, 77769-29-0.

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