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CHLOROPALLADATION OF 1-ARYL-ω-METHYLENEBICYCLO[n.1.0]ALKANES[1a]

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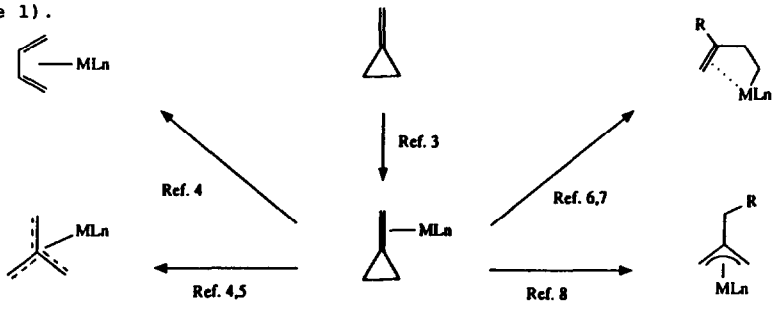
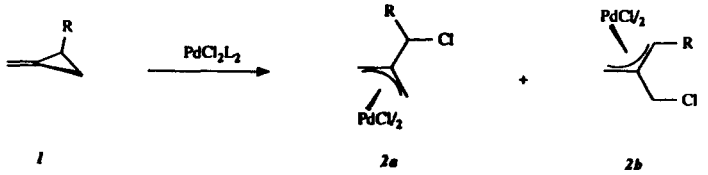
SUMMARY: The chloropalladation of 1-aryl-ω-methylenebicyclo[n.1.0]alkanes affords a mixture of (1-aryl-3-chloro-2-methylenecycloalkyl)- and (3-aryl-3-chloro-2-methylenecycloalkyl)palladium chloride dimers in excellent yield. These products have been characterized by ^{1}H NMR spectroscopy. The regioselectivity of the chloropalladation appears to be dependent on ring strain, steric hinderance and to some extent, the ability of the aryl substituent to stabilize partial positive charge.

The reactivity of strained organic molecules with transition metals is of considerable theoretical and synthetic interest. In particular, the catalytic and stoichiometric organometallic chemistry of methylenecyclopropanes has provided a wealth of novel transformations.[2] Simple η^2-coordination has been observed for 1:1 complexes with iron, rhodium, iridium and platinum.[3] In addition, ring opened complexes of iron,[4] molybdenum,[5] platinum[6] and palladium[7,8] have been reported. Ring opening may occur via cleavage of the C1-C2 bond to furnish η^4-1,3-dienes[4] or via C2-C3 bond cleavage to generate η^4-trimethylenemethane complexes.[4,5] Hydrometallation,[6] carbometallation[7] and halometallation[8] of methylenecyclopropanes can proceed via C1-C2 cleavage to yield 3-butenyl or π-allyl complexes or via C2-C3 cleavage to afford π-allyl complexes (Scheme 1).



Scheme 1.

An example of this latter reaction is the chloropalladation of alkyl- and aryl-substituted methylenecyclopropanes (*1*) which affords π-allyl complexes *2a* and *b*.[8] As part of our program in the application of complexes *2* to organic synthesis,[9,10] we have examined the chloropalladation of a series of 1-aryl-ω-methylenebicyclo[n.1.0]alkanes (*3*).[11]

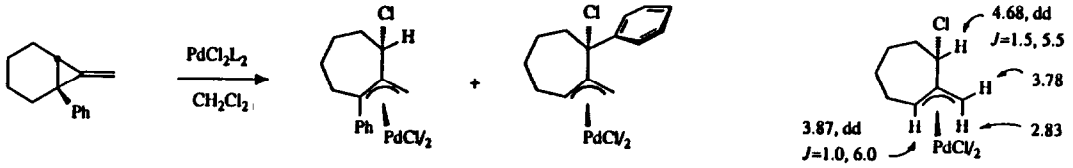


1 *2a* *2b*

RESULTS[12]

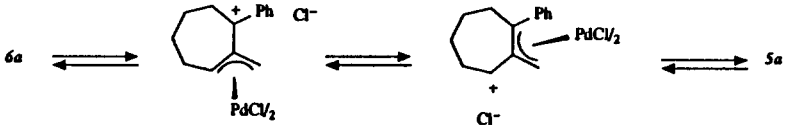
The reaction of 7-methylene-1-phenylbicyclo[4.1.0]heptane (***3a***) with $PdCl_2(CH_3CN)_2$ (***4***) in CH_2Cl_2 gave (3-chloro-2-methylene-1-phenylcycloheptyl)palladium chloride dimer (***5a***) and isomeric (3-chloro-2-methylene-3-phenylcycloheptyl)palladium chloride dimer (***6a***) (2:3 ratio, 96%). The isomer ***6a*** could be separated by fractional crystallization. Heating a mixture of ***5a*** and ***6a*** in CH_3CN at reflux (24h) resulted in conversion of ***6a*** into ***5a*** with excellent mass recovery (98%).

The structure of ***5a*** was assigned by comparison of its NMR spectral data (Table I) with that of 7[8a,13] whose structure had previously been assigned by x-ray crystallographic analysis of the acetylacetonato derivative.[14] The structure of ***6a*** was also assigned by comparison of its ^1H NMR spectral data (Table II) with 7. Notably, the H_1 protons of ***6a*** and 7 appear at approximately the same chemical shift (~3.8 ppm) with a doublet coupling of ~6 Hz. The configuration at C3 (Ph-eq., Cl.-ax.) is based upon a comparison of the chemical shifts of the H_{syn} and H_{anti} protons; an upfield shift of 1.0 and 0.5 ppm respectively for ***6a*** with respect to ***5a***. This upfield shift is presumably due to the anisotropic effect of the neighboring phenyl group.



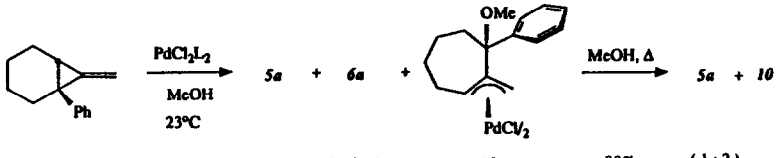
3a 96% ***5a*** (2:3) ***6a*** ***7***

It is clear that chloropalladation of ***3a*** to afford ***5a*** and ***6a*** is under kinetic control. Isomerization of ***6a*** into the more thermodynamically stable ***5a*** involves ionization of the axial chloride to afford the cationic trimethylenemethane ***8a*** (Scheme 2). The cationic trimethylenemethane-Pd(II) system has been predicted by theory,[15] and experimentally shown[16] to be η^3 rather than η^4, with facile migration about the four carbons of the ligand. Capture of the cationic trimethylenemethane isomer ***9a*** by chloride attack generates the more stable product ***5a***.



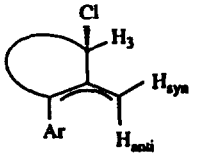
Scheme 2. ***8a*** ***9a***

The reaction of ***3a*** with ***4*** in methanol (23°C) affords ***5a***, ***6a***, and ***10*** (2:3:1 ratio, 94%). Heating this mixture in methanol (65°C, 24h) affords ***5a*** and ***10*** (1:2 ratio, 98%). Pure (3-methoxy-2-methylene-3-phenylcycloheptyl)palladium chloride dimer (***10***) could be isolated by repeated extraction of the more soluble ***5a*** with CH_2Cl_2. The structure of ***10*** was assigned by comparison of its spectral data (experimental section) with that obtained for ***6a***. Notably, stirring the mixture of ***5a*** and ***6a*** (2:3 ratio obtained from chloropalladation of ***3a*** in CH_2Cl_2) in methanol (23°C, 24h) gave only the same ratio of ***5a*** and ***6a***.



3a 94% (2:3:1) ***10*** 98% (1:2)

TABLE I. ^{1}H NMR Data for (1-Aryl-3-chloro-2-methylenecycloalkyl)palladium complexes[a]



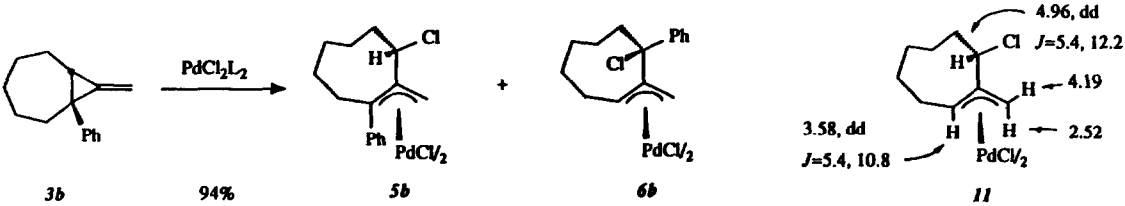
5

compd	H_{syn}	H_{anti}	H_3	Other
5a	3.93 (s)	3.02 (s)	4.87 (dd) [2.4, 5.8]	7.8-7.1 (m; 5H); 2.6-1.2 (m, 8H)
5b	4.44 (s)	2.98 (s)	5.23 (dd) [4.4, 10.4]	7.4-7.1 (br s, 5H); 2.5-1.0 (m, 10H)
5c	4.10 (s)	3.21 (s)	5.34 (d) [6.0]	7.4-7.1 (m, 5H); 2.8-0.8 (m, 8H)
5d	3.96 (s)	3.10 (s)	4.90 (dd) [2.4, 5.6]	7.3-6.9 (m, 4H); 2.26(s, 3H, CH_3); 2.1-1.0 (m, 8H)
5e	3.80 (s)	2.86 (s)	4.88 (dd) [2.6, 5.2]	8.4-8.1, 7.3-6.8 (m, 4H); 2.31 (s, 3H, CH_3); 2.5-1.0 (m, 8H)
5f	3.95 (s)	3.13 (s)	4.90 (dd) [2.5, 6.0]	7.38 (m, 2H); 6.79 (m, 2H); 3.77 (s, 3H, OCH_3); 2.6-0.8 (m, 8H)
5g	3.99 (s)	3.13 (s)	4.92 (dd) [2.6, 5.6]	7.5-6.6 (m, 4H); 3.80 (s, 3H, OCH_3); 3.0-0.7 (m, 8H)
5h	b	2.90 (s)	4.92 (br m)	7.7 (m, 1H); 6.6 (m, 1H); 2.4-1.4 (m); 3.88, 3.84, 3.82 (3 s, 9H)
5i	3.97 (s)	3.07 (s)	4.90 (dd) [2.0, 6.0]	7.3-6.7 (br m, 4H); 2.6-0.5 (m, 8H)
5j	4.02 (s)	3.06 (s)	4.92 (dd) [2.6-5.6]	8.2-8.0, 7.8-7.4 (m, 4H); 2.3-1.0 (m, 8H)

[a]In ppm downfield from $SiMe_4$ (multiplicity: s = singlet, br = broad, d = doublet, dd = doublet of doublets, m = multiplet; integration)[coupling in Hz]; $CDCl_3$ solution. [b]Obscured by methoxy signals.

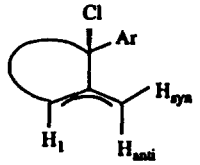
The reaction of 8-methylene-1-phenylbicyclo[5.1.0]octane (*3b*) with *4* in CH_2Cl_2 gave *5b* and *6b* (5:4 ratio, 94%). Heating a sample of the mixture in CH_3CN at reflux (24h) resulted in conversion of *6b* into *5b* with quantitative mass recovery.

The structure of *5b* was assigned by comparison of its ^{1}H NMR spectral data (Table I) with *11*.[13] The H_{syn} and H_{anti} signals of *5b* are shifted downfield from those of *11* by approximately the same magnitude that the H_{syn} and H_{anti} signals of *5a* are shifted downfield from those of *7* (0.2 and 0.3 ppm respectively). The structure of *6b* was assigned by comparison of its ^{1}H NMR spectral data (Table II) with that of *11*. The H_{syn} and H_{anti} signals of *6b* are shifted upfield from those of *11* by approximately the same magnitude as are the H_{syn} and H_{anti} signals of *6b* shifted upfield from those of *7* (0.8 and 0.3 ppm respectively).



3b 94% *5b* *6b* *11*

TABLE II. ^{1}H NMR Data for (3-Aryl-3-chloro-2-methylenecycloalkyl)palladium complexes[a]



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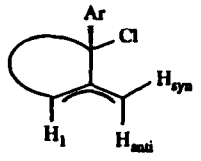

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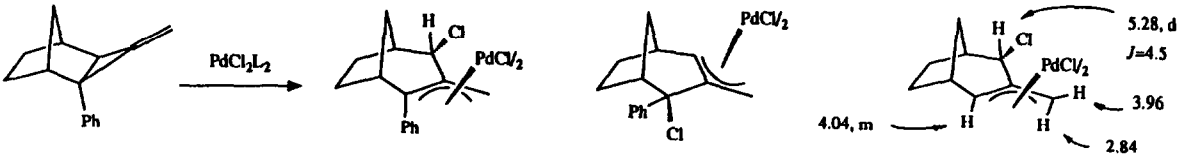
compd	H_{syn}	H_{anti}	H_1	Other
6a	2.92 (s)	2.52 (s)	3.75 (d) [5.6]	8.0-7.2 (m; 5H); 2.5-1.0 (m, 8H)
6b	3.29 (s)	2.75 (s)	4.08 (dd) [4.4, 9.5]	7.4-7.1 (br s, 5H); 5.98 (t, 1H)[8.3]; 2.5-1.0 (m, 10H)
6c	4.06 (s)	3.07 (s)	4.38 (s)	7.4-7.1 (m, 5H); 2.8-0.8 (m, 8H)
6d	2.95 (s)	2.33 (s)	3.73 (d) [6.6]	7.3-6.9 (m, 4H); 2.26(s, 3H, CH_3); 2.1-1.0 (m, 8H)
13d	3.47 (s)	2.80 (s)	4.23 (t)	7.76, 7.12 (AA'BB', 4H); 2.32 (s, 3H, CH_3); 2.3-1.2 (m, 8H)
6e	3.12 (s)	2.55 (s)	3.95 (d) [5.2]	8.4-8.1, 7.3-6.8 (m, 4H); 2.34 (s, 3H, CH_3); 2.5-1.0 (m, 8H)
13f	3.49 (s)	2.81 (s)	4.23 (t) [8.5]	7.75, 6.85 (AA'BB', 4H)[J_{AB} = 8.8] 6.22 (t, J = 6.6); 3.78 (s, 3H, OCH_3); 2.5-1.2 (m, 8H)
6g	3.21 (s)	2.63 (s)	4.16 (br m)	7.4-6.9 (m); 6.06 (t, 1H)[7]; 3.88 (s, 3H, OCH_3); 2.4-1.5 (m, 8H)
6h	3.25 (s)	2.64 (s)	4.09 (br m)	7.7 (m, 1H); 6.6 (m, 1H); 2.4-1.4 (m); 3.86, 3.84 (2 s, 9H)
13i	3.40 (s)	2.79 (s)	4.23 (t) [7.2]	7.6 (m); 7.0 (m); 6.23 (t, 1H)[7]; 2.4-1.5 (m, 8H)
6j	2.82 (s)	2.51 (s)	3.77 (d) [5.8]	8.2, 7.7-7.3 (m, 4H); 2.5-1.4 (m, 8H)

[a]In ppm downfield from $SiMe_4$ (multiplicity: s = singlet, br = broad, d = doublet, dd = doublet of doublets, m = multiplet; integration)[coupling in Hz]; $CDCl_3$ solution.

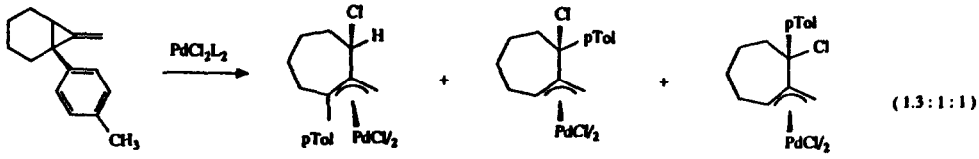
The reaction of *exo*-3-methylene-2-phenyltricyclo[3.2.1.$0^{2,4}$]octane (*3c*) with *4* in CH_2Cl_2 gave *5c* and *6c* (1:2 ratio, 95%). The structures of *5c* and *6c* were assigned by comparison of their ^{1}H NMR spectral data (Tables I and II) with that of *12*.[13]



3c 95% *5c* (1:2) *6c* *12*

The reaction of 1-(4'-methylphenyl)-7-methylenebicyclo[4.1.0]heptane (*3d*) with *4* in CH_2Cl_2 gave *5d*, *6d* and *13d* (1.3:1:1 ratio, 74%). Heating a sample of the mixture in CH_3CN at reflux (21h) gave exclusively *5d* with quantitative mass recovery. The structure of *5d* was assigned by comparison of its NMR spectral data (Table I) with that of *5a*. The structure of *6d* was assigned by comparison of its ^{1}H NMR spectral data (Table II) with that of *6a*. The structure of diastereomer *13d* was assigned by comparison of its ^{1}H NMR spectral data (Table II) with *6d* and 7. In particular, while the H_{syn} and H_{anti} signals of *6d* are significantly shifted upfield with

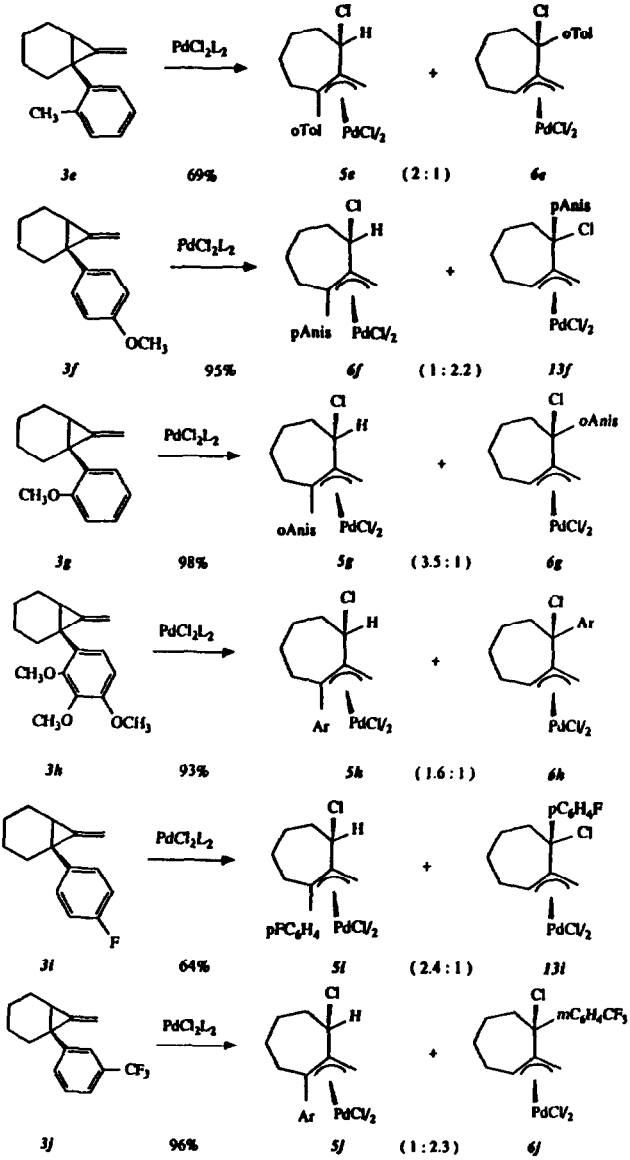
respect to **5d** due to the anisotropy of the phenyl substituent, the H_{syn} and H_{anti} of **13d** are not shifted as far upfield.



3d 74% **5d** **6d** **13d** (1.3:1:1)

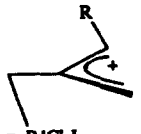
In a similar fashion, the chloropalladation of **3e-j** gave the π-allyl complexes **5e-j**, **6e-j**, and **13f,i** (Scheme 3) whose structural assignments are based upon comparison of their ^1H NMR spectral data (Tables I and II) with that of **5a**, **6a**, and **13d**.

Scheme 3.



DISCUSSION

It has been proposed that the chloropalladation of *1* proceeds via i) initial coordination of $PdCl_2$ to the less hindered face of the methylenecyclopropane, followed by ii) disrotatory ring opening of the C2-C3 bond[17] and iii) suprafacial transfer of the chloride ligand to either C2 or C3.[8a] Extended Huckel calculations indicate that the Pd-metal slips away from the central carbon (ie. $\eta^2 \rightarrow \eta^1$) prior to/or during chloride transfer.[8a] It should be noted that slippage to η^1 would create a cyclopropyl carbocation species which would open in an allowed disrotatory fashion. However the intermediacy of a discrete zwitterionic η^1-trimethylenemethane species such as *14* was ruled out on the basis of the stereospecific, suprafacial chloride ligand transfer as well as by the failure to trap such an intermediate in a nucleophilic solvent. The exact timing of disrotatory ring opening and chloride transfer is not known, however it may depend upon "geometrical constraints imposed by substituents on the methylenecyclopropane ring."[8a]



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The structure of products *5* and *6* reflect *apparent trans* addition of Pd-Cl across the cyclopropane ring of compounds *3*. However in order to be consistent with the mechanism for the chloropalladation of *cis*- and *trans*-9-methylenebicyclo[6.1.0]nonane,[8a] it is believed that the products which arise via dis-in-*cis*-addition (*5'* and *13*) undergo a rapid $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerization and/or ring inversion to afford the structure with the most stable configuration/conformation.[8a,13] Evidence to support the *cis*-addition mechanism comes from the chloropalladation of *3c*. The products *5c* and *6c* are both assigned the Cl-endo configuration. This indicates that Cl is delivered to the less hindered face of the methylenecyclopropane ring. This is the face which should coordinate to $PdCl_2$ in the initial step of the mechanism (*vide supra*).

For the (1-aryl-3-chloro-2-methylenecyclo*heptyl*)palladium chloride dimers (*5a, d-j*) the most stable structure has the C3 chloride cubstituent in an axial position; *trans* to the Pd atom. The 3-chloro-2-methylene-1-phenylcyclo*octyl*)palladium chloride dimer (*5b*) has the same configuration at C3, however the cyclooctyl ring adopts a conformer similar to that of *11*. A rationale for the stability of the different conformers for the 7- and 8-membered rings has previously been presented.[13] For the (3-aryl-3-chloro-2-methylenecycloalkyl)palladium complexes the situation is considerably more complex, and an unequivocal rationale for the differential stability of the $\eta^3 \rightarrow \eta^1 - \eta^3$ isomers *6* and *13* is not possible. For example, it has been shown that for geminally substituted phenyl*cyclohexanes*, the energy difference between the phenyl equatorial and phenyl axial conformers depends upon the presence of substituents α to the phenyl, as well as substituents present on the aryl ring.[18]

The chloropalladation of *3a* in methanol (23°C) affords *5a*, *6a*, and a methoxy substituted product (*10*). It should be noted that the methanolysis of *6a* to afford *10* requires more vigorous

reaction conditions (65°C). Therefore it is clear that the product ***10*** formed from ***3a*** must arise from a competitive addition of palladium and methanol across the cyclopropane bond in a *cis* fashion, followed by a rapid $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerization, *or* by nucleophilic attack of methanol on an π-organopalladium species in a *trans* fashion. The unambiguous studies of the stereochemistry of alkoxypalladation have shown only *trans* attack.[19] The regiospecific addition of methanol to the phenyl substituted cyclopropane carbon of ***3a*** strongly implies an intermediate involving some carbocation character.

The present results indicate that there is a slight kinetic preference for chloride transfer to the phenyl substituted cyclopropane carbon (***6a***) as opposed to transfer to the unsubstituted cyclopropane carbon (***5a***). This selectivity is in marked contrast to the lack of selectivity observed for chloropalladation of 2-phenyl- and 2,2-diphenylmethylenecyclopropane.[8b] The preference for chloride transfer to the phenyl substituted carbon of ***3*** appears to be dependent on ring strain; for the less strained ***3b*** nearly equal amounts of products ***5b*** and ***6b*** are obtained, while for the more highly strained ***3c*** there is an increased preference for Cl transfer to the phenyl substituted carbon (ie. ***6c*** vs. ***5c***). This dependence upon ring strain should reflect the relative timing of the ring opening and of Cl transfer. For the less strained system, ring opening and Cl transfer occur with comparable rates, however, for the more strained structures, ring opening is more rapid than the transfer of Cl, and thus greater buildup of partial positive charge occurs for the more strained ring systems. The results for the chloropalladation of 1-aryl-7-methylenebicyclo[4.1.0]heptanes bearing a *para*-substituent (ie. ***3d***, ***3f***, ***3i***) are consistent with the slight development of partial positive charge.

Perhaps more dramatic is the effect of steric hindrance on the regioselectivity of chloride transfer. Chloropalladation of compounds bearing an *ortho* substituent (ie. ***3e***, ***3g***) gave predominantly the product resulting from attack of chloride at the unsubstituted cyclopropane carbon (***5e***, ***5g***). Interestingly, chloropalladation of ***3h***, a compound which bears both an *ortho* substituent as well as an electron donating *para* substituent, affords the product from chloride transfer to the unsubstituted carbon (***5h***) as the major product (1.6:1 ratio). Thus steric hindrance has a greater influence on the regioselectivity than does electronic effects.

In summary, the chloropalladation of 1-aryl-ω-methylenebicyclo[n.1.0]alkanes proceeds via cleavage of the C2-C3 cyclopropane bond to afford aryl substituted (3-chloro-2-methylenecycloalkyl)palladium chloride dimers in good to excellent yields. The regioselectivity for chloride transfer appears to depend upon ring strain and steric hindrance, and to a lesser extent upon the ability of the aryl substituent to stabilize partial positive charge. The application of complexes ***5*** and ***6*** to organic synthesis is the subject of the following paper.

EXPERIMENTAL

General Data. All IR spectra were recorded on a Perkin Elmer 700 spectrometer and were calibrated against the 1601 cm^{-1} peak of polystyrene. All 60 MHz ^1H NMR and 15 MHz $^{13}C(^1H)$ NMR spectra were recorded on a Varian EM360L or a JEOL FX60Q spectrometer; chemical shifts are reported in ppm downfield of TMS and couplings are reported in hertz. All 300 MHz ^1H NMR spectra were recorded on a GE QE-300 spectrometer. Melting points were obtained using a Mel-Temp melting point apparatus and are uncorrected. Microanalyses were sent to Midwest Microlab, LTD., Indianapolis, IN.

All organometallic reactions were run under an atmosphere of nitrogen. Spectrograde solvents were used without further purification except for diethyl ether which was distilled

from sodium benzophenone ketyl. Preparative thin layer chromatography plates (20 x 20 cm) were prepared from a slurry of silica gel (GF-254, type 60, 30g) in water (70 mL) and were dried (125°C) for 24h prior to use.

Arylcycloalkenes were prepared from the appropriate aryl bromide, via Grignard formation and condensation with the appropriate cycloalkanone. The resultant crude cycloalkanols were dehydrated by treatment with a catalytic amount of crystalline iodine, or *p*TsOH in refluxing benzene with azeotropic removal of water. The arylcycloalkenes are all known compounds.[20]

1-Aryl-ω-methylenebicyclo[n.1.0]alkanes were prepared from the corresponding arylcycloalkene by addition of chloromethylcarbene (Cl_2HCCH_3, *n*BuLi, -10°C) followed by dehydrohalogenation (tBuOK, DMSO, 90°C) according to the method of Arora and Binger.[21] Prepared in this manner were: 7-methylene-1-phenylbicyclo[4.1.0]heptane (***3a***, 65%, bp 39-40°C/0.025 mm Hg); 8-methylene-1-phenylbicyclo[5.1.0]octane (***3b***, 31%, bp 71-79°C/0.24 mm Hg); *exo*-3-methylene-2-phenyltricyclo-[3.2.1.$0^{2,4}$]octane (***3c***, 11%, bp 75-77°C/0.55 mm Hg); 1-(4'-methylphenyl)-7-methylenebicyclo-[4.1.0]heptane (***3d***, 26%, bp 75°C/0.18 mm Hg); 1-(2'-methylphenyl)-7-methylenebicyclo[4.1.0]-heptane (***3e***, 15%, bp 85°C/0.20 mm Hg); 1-(4'-methoxyphenyl)-7-methylenebicyclo[4.1.0]heptane (***3f***, 7%, bp 81°C/0.80 mm Hg); 1-(2'-methoxyphenyl)-7-methylenebicyclo[4.1.0]heptane (***3g***, 9%, mp 34-35°C); 1-(2',3',4'-trimethoxyphenyl)-7-methylenebicyclo[4.1.0]heptane (***3h***, 53%, mp 37-38°); 1-(4'-fluorophenyl)-7-methylenebicyclo[4.1.0]heptane (***3i***, 2%, bp 45°C/0.07 mm Hg); 1-(3'-trifluoromethylphenyl)-7-methylenebicyclo[4.1.0]heptane (***3j***, 60%, bp 70°C/0.23 mm Hg). Pertinent spectral data for compounds ***3a-j*** appear in Table III.

TABLE III. ^{1}H NMR Data for 1-Aryl-ω-methylenebicyclo[n.1.0]alkanes[a]

compd	H_{Aryl}	$H_{methylene}$	H_{alkyl}	Other
3a	7.4-7.1 (br s, 5H)	5.50 (m; 2H)	2.2-1.2 (m; 9H)	-
3b	7.4-7.0 (br s; 5H)	5.41 (br s; 1H) 5.30 (br s; 1H)	2.5-1.2 (m; 11H)	-
3c	7.2-7.0 (s; 5H)	5.22 (m; 2H)	2.0-1.0 (m; 7H)	2.75 (br s; bridgehead H) 2.16 (br s; bridgehead H)
3d	7.3-6.8 (AA'BB')	5.45 (br s; 2H)	2.1-1.2 (m; 9H)	2.27 (s; 3H; CH_3)
3e	7.2-6.8 (m; 4H)	5.57 (br s; 1H) 5.35 (br s; 1H)	2.0-1.0 (m; 9H)	2.36 (s; 3H; CH_3)
3f	7.3-6.6 (AA'BB', J_{AB}=9)	5.39 (m; 2H)	2.2-1.1 (m; 9H)	3.63 (s; 3H; OCH_3)
3g	7.4-6.6 (complex m; 4H)	5.65 (br s; 1H) 5.45 (br s; 1H)	2.1-1.2 (m; 9H)	3.81 (s; 3H; OCH_3)
3h[b]	6.50, 6.35 (J_{AB}=8, 2H)	5.54 (br s; 1H) 5.36 (br s; 1H)	2.2-0.7	3.88 (s; 3H, OCH_3) 3.72 (s; 6H, OCH_3)
3i	7.4-6.7 (complex m; 4H)	5.50 (m; 2H)	2.2-1.1 (m; 9H)	-
3j[b]	7.6-7.4 (m; 4H)	5.53 (m; 2H)	2.3-0.8 (m; 9H)	-

[a] In ppm downfield from internal $SiMe_4$ (multiplicity: s = singlet, br s = broad singlet, m = multiplet; integration); $CDCl_3$ solution unless otherwise noted. [b] CCl_4.

General Procedure for Chloropalladation of 1-Aryl-ω-methylenebicyclo[n.1.0]alkanes. To a solution of $PdCl_2(CH_3CN)_2$ (~0.25 mmol) in CH_2Cl_2 (30 mL) was added, in one portion, a solution of the 1-aryl-ω-methylenebicyclo[n.1.0]alkane (1 molar equiv.) in CH_2Cl_2 (8 mL). The red-orange solution rapidly turned pale yellow, and the solution was stirred for 1h. The solvent was evaporated and the product dried under high vacuum. Pertinent ^{1}H NMR data for the products appear in Tables I and II. The following 1-aryl-ω-methylenebicyclo[n.1.0]alkanes were treated in the above fashion:

Chloropalladation of ***3a***. The product was identified by NMR spectroscopy (Tables I and II) as consisting of ***5a*** and ***6a*** (2:3 ratio, 96%). Fractional crystallization of the mixture (CH_2Cl_2/hexanes) afforded pure ***6a*** as a pale yellow solid: mp 158°C dec. Anal. Calcd for $[C_{14}H_{16}Cl_2Pd]_2$: C, 46.50; H, 4.46. Found C, 46.22; H, 4.52. A sample of the mixture (0.50 g)

was heated at reflux in CH_3CN (100 mL) for 24h. Removal of the solvent *in vacuo* gave a golden yellow solid, identified as exclusively ***5a*** by ^1H NMR spectroscopy (0.49 g, 98%): mp 185°C dec. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 142.9, 128.9, 128.3, 127.3, 121.3, 98.6, 64.2, 63.4, 40.2, 37.7, 26.9, 25.0; Anal. Calcd for $[C_{14}H_{16}Cl_2Pd]_2$: C, 46.50; H, 4.46. Found C, 46.23; H, 4.57.

Chloropalladation of ***3a*** in methanol. To a solution/suspension of ***4*** (0.21 g, 0.81 mmol) in methanol (15 mL) was added ***3a*** (0.15 g, 0.81 mmol). The red-orange solution immediately began to pale. The reaction mixture was stirred for 1h, and then the solvent was removed under reduced pressure and dried *in vacuo* to afford a yellow powder (0.27 g, 94%). The product was identified by ^1H NMR spectroscopy as a mixture of ***5a***, ***6a***, and ***10*** (2:3:1). The sample was taken up in methanol (25 mL) and heated at a gentle reflux for 24h. The reaction mixture was cooled and the solvent removed under reduced pressure to afford a pale yellow powder. NMR spectroscopy indicated that this consisted of ***5a*** and ***10*** (1:2 ratio, 98%). A pure sample of ***10*** could be obtained as an off-white powder by repeated extraction from the mixture of the more soluble ***5a*** with CH_2Cl_2. ***10***: mp 190°C dec.; ^1H NMR ($CDCl_3$) δ 8.0-7.1 (m, ArH, 5H), 3.81 (d, J = 5.6, 1H), 3.28 (s, 3H), 3.02 (s, 1H), 2.62 (s, 1H), 2.5-1.0 (m, 8H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 142.4, 129.3, 128.2, 127.4, 126.9, 84.5, 82.6, 63.2, 52.2, 30.4, 29.8, 27.8, 24.1; Anal. Calcd for $[C_{15}H_{19}OPdCl]_2$: C, 50.44; H, 5.36. Found: C, 48.86; H, 5.36.

Chloropalladation of ***3b***. The product was identified by NMR spectroscopy (Tables I and II) as consisting of ***5b*** and ***6b*** (5:4 ratio, 94%). A sample of the mixture (0.10 g) was heated at reflux in CH_3CN (30 mL) for 24h. Removal of the solvent *in vacuo* gave a golden yellow solid, identified as exclusively ***5b*** by ^1H NMR spectroscopy (0.10 g, 100%): mp 130-135°C; Anal. Calcd for $[C_{15}H_{18}Cl_2Pd]_2$: C, 47.95; H, 4.83. Found C, 46.63; H, 4.96.

Chloropalladation of ***3c***. The product was identified by NMR spectroscopy (Tables I and II) as consisting of ***5c*** and ***6c*** (1:2 ratio, 95%). The isomeric products were separated by preparative TLC with benzene-hexanes elution (3:1). ***5c***: Rf = 0.72, mp 139°C dec. Anal. Calcd for $[C_{15}H_{16}Cl_2Pd]_2$: C, 48.22; H, 4.31. Found C, 48.64; H, 4.63. ***6c***: Rf = 0.36, mp 177°C dec. A sample of the mixture was heated at reflux in CH_3CN (30 mL) for 24h. Removal of the solvent *in vacuo* gave a golden yellow solid, identified as exclusively ***5c*** by ^1H NMR spectroscopy.

Chloropalladation of ***3d***. The crude product was passed through a short bed of silica with CH_2Cl_2 elution. The product was identified by NMR spectroscopy (Tables I and II) as consisting of ***5d***, ***6d*** and ***13d*** (1.3:1:1 ratio, 74%). Isomer ***13d*** could be isolated by preparative TLC with benzene elution (Rf = 0.45). A sample of the mixture (0.11 g) was heated at reflux in CH_3CN (30 mL) for 24h. Removal of the solvent *in vacuo* gave a golden yellow solid, ***5d***: mp 136°C dec.; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 140.0, 137.2, 129.1, 128.9, 121.3, 64.1, 63.5, 40.3, 37.8, 26.9, 25.2, 21.3; Anal. Calcd for $[C_{15}H_{18}Cl_2Pd]_2$: C, 47.95; H, 4.83. Found C, 48.17; H, 4.87.

Chloropalladation of ***3e***. The crude product was passed through a short bed of silica with CH_2Cl_2 elution. The product thus obtained was identified by NMR spectroscopy (Tables I and II) as consisting of ***5e*** and ***6e*** (2:1 ratio, 69%). A sample of the mixture (0.13 g) was heated at reflux in CH_3CN (30 mL) for 24h. Removal of the solvent *in vacuo* gave a golden yellow solid, identified as exclusively ***5e*** by ^1H NMR spectroscopy (0.12 g, 92%). An analytical sample was recrystallized from benzene: mp 145°C dec.; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 142.5, 134.8, 130.8, 127.0, 126.4, 125.7, 121.5, 63.9, 62.3, 39.8, 38.2, 26.8, 24.2, 21.1; Anal. Calcd for $[C_{15}H_{18}Cl_2Pd]_2 \cdot C_6H_6$: C, 52.14; H, 5.10. Found C, 51.94; H, 5.46.

Chloropalladation of ***3f***. The product was identified by NMR spectroscopy (Tables I and II) as consisting of ***5f*** and ***6f*** (1:2.2 ratio, 95%). The isomeric products were separated by preparative TLC with benzene elution. ***6f***: Rf = 0.51, mp 137°C dec. Anal. Calcd for $[C_{15}H_{18}OCl_2Pd]_2 \cdot \frac{1}{3}C_6H_6$: C, 47.49; H, 4.73. Found C, 47.39; H, 4.51. A sample of the mixture (0.10 g) was heated at reflux in CH_3CN (30 mL) for 24h. Removal of the solvent *in vacuo* gave a golden yellow solid, identified as ***5f*** by ^1H NMR spectroscopy (0.10 g, 100%): mp 140°C dec.

Chloropalladation of ***3g***. The product was identified by NMR spectroscopy (Tables I and II) as consisting of ***5g*** and ***6g*** (3.5:1 ratio, 98%). The isomer ***5g*** could be isolated by preparative TLC with benzene elution (Rf = 0.71). ***5g***: mp 144°C dec. Anal. Calcd for $[C_{15}H_{18}OCl_2Pd]_2$: C, 46.02; H, 4.64. Found C, 46.47; H, 4.72.

Chloropalladation of ***3h***. The product was identified by NMR spectroscopy (Tables I and II) as consisting of ***5h*** and ***6h*** (1.6:1 ratio, 93%): mp 98°C dec. Anal. Calcd for $[C_{17}H_{22}O_3Cl_2Pd]_2$: C, 45.21; H, 4.91. Found C, 46.20; H, 4.91.

Chloropalladation of ***3i***. The crude product was passed through a short bed of silica with CH_2Cl_2 elution. The product thus obtained was identified by NMR spectroscopy (Tables I and II) as consisting of ***5i*** and ***6i*** (2.4:1 ratio, 64%). A sample of the mixture (0.14 g) was heated at

reflux in CH_3CN (50 mL) for 24h with no change in composition. The regioisomers could be separated by preparative TLC with benzene-hexanes-ethyl acetate (10:7:3) as eluent. **5i**: Rf = 0.83; mp 170°C dec.; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 162.2 (J_{CF} = 245.0), 138.8, 130.6 (J_{CF} = 8.5), 115.4 (J_{CF} = 22.0), 121.7, 64.4, 63.4, 40.1, 37.7, 27.0, 24.9; ***6i***: Rf = 0.74.

Chloropalladation of ***3j***. The product was identified by NMR spectroscopy (Tables I and II) as consisting of ***5j*** and ***6j*** (1:2.3 ratio, 96%). A sample of the mixture (0.12 g) was heated at reflux in CH_3CN (30 mL) for 24h. Removal of the solvent *in vacuo* gave a golden yellow solid, identified as ***5j*** by ^1H NMR spectroscopy (0.11 g, 92%): mp 165-170°C dec.; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 143.7, 132.8, 132.3, 129.0, 125.3, 124.4, 121.7, 96.5, 64.8, 63.3, 40.1, 37.6, 27.2, 24.8; Anal. Calcd for $[C_{15}H_{15}F_3Cl_2Pd]_2$: C, 41.94; H, 3.52. Found C, 42.95; H, 3.69.

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REFERENCES AND NOTES

1) a) Presented, in part, by JTN at the ACS Undergraduate Research Symposium, 189th National ACS Meeting, Miami Beach, FL, April 28-May 3, 1985, Division of Chemical Education, Paper No. 43; b) ACS-PRF summer Undergraduate Research Fellow, 1984.
2) Binger, P.; Buch, H.M. *Top. Curr. Chem.*, 1987, 135, 77-151.
3) Green, M.; Howard, J.A.K.; Hughes, R.P.; Kellett, S.C. *J. Chem. Soc., Dalton Trans.*, 1975, 2007-14.
4) Pinhas, A.R.; Samuelson, A.G.; Risemberg, R.; Arnold, E.V.; Clardy, J.; Carpenter, B.K. *J. Am. Chem. Soc.*, 1981, 103, 1668-75; Whitesides, T.H.; Slaven, R.W. *J. Organometal. Chem.*, 1974, 67, 99-108; Noyori, R.; Nishimura, T.; Takaya, H. *J. Chem. Soc. (D)*, 1969, 89.
5) Allen, S.R.; Barnes, S.G.; Green, M.; Moran, G.; Trollope, L.; Murrall, N.W.; Welch, A.J.; Sharaiha, D.M. *J. Chem. Soc., Dalton Trans.*, 1984, 1157-69.
6) Phillips, R.L.; Puddephatt, R.J. *J. Chem. Soc., Dalton Trans.*, 1978, 1736-9.
7) Larock, R.C.; Varaprath, S. *J. Org. Chem.*, 1984, 49, 3432-5; Balme, G.; Fournet, G.; Gore, J. *Tetrahedron Lett.*, 1986, 3855-8; Donaldson, W.A.; Brodt, C.A. *J. Organometal. Chem.*, 1987, 330, C33-C36; Fournet, G.; Balme, G.; Gore, J. *Tetrahedron*, 1988, 44, 5809-20.
8) a) Albright, T.A.; Clemens, P.R.; Hughes, R.P.; Hunton, D.E.; Margerum, L.D. *J. Am. Chem. Soc.*, 1982, 104, 5369-79; b) Dallas, B.K.; Hughes, R.P.; Schumann, K. *Ibid.*, 1982, 104, 5380-3; c) Clemens, P.R.; Hughes, R.P.; Margerum, L.D. *J. Am. Chem. Soc.*, 1981, 103, 2428-30; d) Hughes, R.P.; Hunton, D.E.; Schumann, K. *J. Organometal. Chem.*, 1980, 184, C67-C69.; e) Dallas, B.K.; Hughes, R.P. *Ibid.*, 1980, 184, C67-C69; f) Noyori, R.; Takaya, H. *J. Chem. Soc., Chem. Comm.*, 1969, 77.
9) Donaldson, W.A.; Grief, V.J. *Tetrahedron Lett.*, 1986, 2345-8; Donaldson, W.A.; Wang, J.; Cepa, V.G.; Suson, J.D. *J. Org. Chem.*, accepted for publication.
10) Donaldson, W.A.; Stepuszek, D.J.; Gruetzmacher, J.A. *Tetrahedron*, following paper in this issue.
11) A preliminary account of some of this work has appeared: Donaldson, W.A. *J. Organometal. Chem.*, 1984, 269, C25-C28.
12) All compounds described in this paper are racemic mixtures of enantiomers. For simplicity only one enantiomer is diagrammed.
13) Donaldson, W.A. *Organometallics*, 1986, 5, 223-30.
14) Hughes, R.P.; Day, C.S. *Organometallics*, 1982, 1, 1221-5.
15) Albright, T.A. *J. Organometal. Chem.*, 1980, 198, 159-68.
16) Lukas, J.; Kramer, P.A. *J. Organometal. Chem.*, 1971, 31, 111-8.
17) In the bicyclo[4.1.0]heptane ring system, the disrotatory opening occurs in a dis-in fashion due to geometrical constraints.
18) Hodgson, D.J.; Rychlewska, U.; Eliel, E.L.; Manoharan, M.; Knox, D.E.; Olefirowicz, E.M. *J. Org. Chem.*, 1985, 50, 4838-43; Eliel, E.L.; Manoharan, M.; Levine, S.G.; Ng, A. *Ibid.*, 1985, 50, 4978-80.
19) Stille, J.K.; Morgan, R.A. *J. Am. Chem. Soc.*, 1966, 88, 5135-41; Wiger, G.; Albelo, G.; Rettig, M.F. *J. Chem. Soc., Dalton, Trans.*, 1974, 2242-7; Hall, S.S.; Akermark, B. *Organometallics*, 1984, 3, 1745-8; The "*cis*-methoxypalladation" of dehydro-β-pinene has been reported, however the product which reflects apparent *cis*-addition might arise via *trans*-addition followed by $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerization: Hosokawa, T.; Imada, Y.; Murahashi, S.-I. *Tetrahedron Lett.*, 1982, 3373-4.
20) Core, S.K.; Lotspeich, F.J. *J. Med. Chem.*, 1969, 12, 334-6; Balsamo. A.; Battistini, C.; Crotti, P.; Macchia, B.; Macchia, F. *Gazz. Chim. Ital.*, 1976, 106, 77-83; Ginsburg, D.; Pappo, R. *J. Am. Chem. Soc.*, 1953, 75, 1094-7; Kleinfelter, D.C.; Dye, T.E.; Mallory, J.E.; Trent, E.S. *J. Org. Chem.*, 1967, 32, 1743-41.
21) Arora, S.; Binger, P. *Synthesis*, 1977, 682-3.