Reactions of Acetylenes with Noble-Metal Halides. X.[1,2] Reaction of Phenylpalladium Chloride with 2-Butyne and the Structure and Stereochemical Nonrigidity of a *Dihapto*cyclopentadiene, [$\overline{C_5Me_5CH(R)CH_2Pd}$(acac)]

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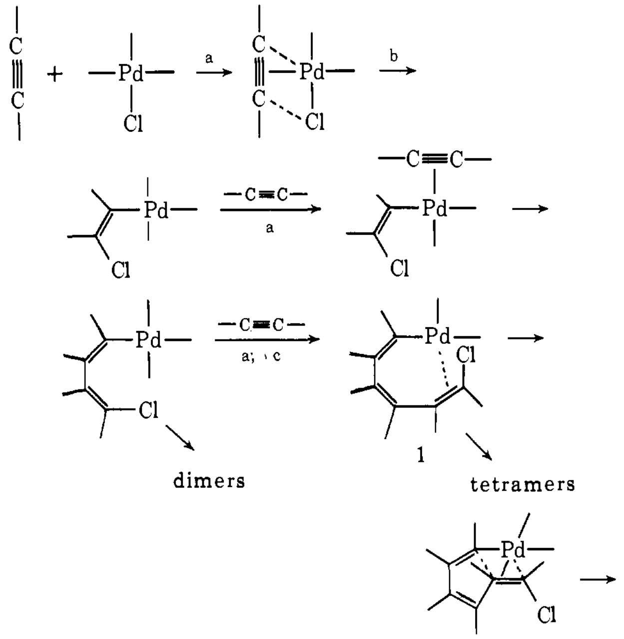
Abstract: Reaction of 2-butyne, diphenylmercury, and dichlorobis(benzonitrile)palladium gave the complex **2a** which was shown by spectroscopic methods and degradation reactions to have the structure [$\overline{C_5Me_5CHPhCH_2Pd}$-Cl]$_2$. This was confirmed by an X-ray crystal structure determination of the closely related complex **3b**. The complex crystallizes in the triclinic system with space group $P\bar{1}$ containing two molecules of two optical enantiomers in the unit cell. The structure consists of a pentamethylcyclopentadiene, *only one double bond* of which is coordinated to the palladium, which is also σ bonded *via* a -CH_2CH(*p*-tolyl)- bridge to the 5 position of the cyclopentadiene. Bond lengths and angles are normal for the groups involved. In solution the complex **3a** exhibits stereochemical nonrigidity as shown by the variation in nmr spectrum with temperature. This behavior is interpreted in terms of the metal moving across the cyclopentadiene ring from one double bond to the other. The chloro complexes **2** also undergo a similar rearrangement and, in addition, a slower irreversible rearrangement to the *trihapto*bicyclo[3.2.0]heptenyl complexes **8**. Reaction of **8a** with cyanide gave a bicyclo[3.2.0]heptene, shown to be different from the norbornenes from the Diels–Alder reaction of styrene and pentamethylcyclopentadiene. On thermal decomposition **2a**, **3a**, and **8a** all gave *trans*-$C_5Me_5CH{=}CHPh$. The mechanism of the formation of **2a** in the direct reaction and also from **1** is discussed.

Over the past few years we have been investigating the products and mechanisms of the reactions of palladium chloride and disubstituted acetylenes. We have suggested a stepwise mechanism for the oligomerization reactions that are observed which involves a series of cis ligand migrations ("insertion reactions") of Pd–X onto the coordinated acetylene.[4–6]

For example, in the reaction of 2-butyne with palladium chloride[7] we proposed that the rate-determining step in the formation of the product, **1**, was the insertion of the butyne into a Pd–Cl bond (step a) and that the succeeding complexation and insertion reactions (steps b and c) into Pd-vinyl σ bonds were fast.[4] By analogy then we expect other disubstituted acetylenes to react similarly, the extent of the overall reaction being determined by the sizes of the acetylenic substituents with the smaller ones such as methyl giving the higher oligomers; in the case of 2-butyne trimer complexes and some uncharacterized tetramers are obtained.

If this argument is correct, then it should be possible to carry out this reaction using alkyl- or arylpalladium compounds as substrates even more easily since in that case the initial insertion is also into a Pd–C σ bond because Pd–C bonds are usually more reactive than Pd–Cl bonds.



The reaction we chose is one based on the work of Heck who showed that a phenylpalladium species (arbitrarily designated as "PhPdCl" here), formed *in situ* by reaction of palladium chloride and diphenylmercury, would add to olefins.[8] The exact products depend on the olefin chosen; a typical reaction sequence is

$$PdCl_2 + Ph_2Hg \longrightarrow \text{"PhPdCl"} + PhHgCl$$
$$\text{"PhPdCl"} + RCH{=}CH_2 \longrightarrow PhCH_2CH(R)PdCl$$
$$PhCH_2CH(R)PdCl \longrightarrow PhCH{=}CHR + HPdCl$$
$$HPdCl \longrightarrow HCl + Pd$$

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[1] Part IX: H. Reinheimer, J. Moffat, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 92, 2285 (1970).

[2] Part of this work has already been communicated: C. Calvo, T. Hosokawa, H. Reinheimer, and P. M. Maitlis, *J. Amer. Chem. Soc.*, **94**, 3237 (1972); P. M. Maitlis, Plenary Lecture, XIVth International Conference on Coordination Chemistry, Toronto; *Pure Appl. Chem.*, **33**, 489 (1973).

[3] All correspondence should be addressed to this author at the Department of Chemistry, The University, Sheffield S3 7HF, England.

[4] H. Dietl, H. Reinheimer, J. Moffat, and P. M. Maitlis, *J. Amer. Chem. Soc.*, **92**, 2276 (1970).

[5] P. M. Maitlis, *Pure Appl. Chem.*, **30**, 427 (1972).

[6] P. M. Maitlis, "The Organic Chemistry of Palladium," Vol. II, Academic Press, New York, N. Y., 1971, pp 47–58.

[7] Dichlorobis(benzonitrile)palladium is the usual starting material; it can be conveniently regarded as simply a source of soluble $PdCl_2$.[4]

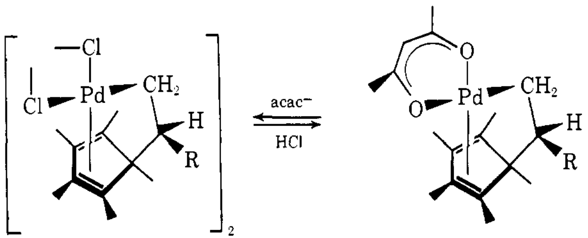
[8] R. F. Heck, *J. Amer. Chem. Soc.*, **90**, 5518, 5526, 5531, 5535, and 5538 (1968).

We have applied this reaction in the synthesis of the complex **2a** which is obtained in 45% yield from the reaction of 2-butyne, diphenylmercury, and dichlorobis(benzonitrile)palladium (in a 7:1:1 molar ratio) in either benzene or, preferably, dichloromethane. In addition, a 3% yield of a tetramer complex, formally $[Ph(C_2Me_2)_4PdCl]_2$, was isolated, but this has not yet been characterized; the remaining product consisted of a dark brown polymeric and intractable solid.

The analytical data on **2a** initially suggested a formula $[Ph(C_2Me_2)_3PdCl]_2$ and, by analogy with **1**, a similar structure with phenyl in place of the vinylic chlorine. However, while **1** clearly shows the presence of six inequivalent methyl groups in the nmr spectrum, that of **2a** under optimum conditions (see below) only shows five, and this obviously rules out a similar structure. Based on this result, the degradation reactions described in the following paper,[9] as well as an analysis of the temperature variation of the nmr spectra of **2a** and its analogs, we proposed the structure shown for the complex.

In order to confirm this and also to define the stereochemistry of the complex, we carried out an X-ray structure determination. Unfortunately, neither crystals of **2a** nor **2b** (made by an analogous reaction from di-*p*-tolylmercury) were suitable for analysis; however, good crystals of the acetylacetonate of the *p*-tolyl complex, **3b**, could be grown and the structure was determined for this molecule. Since the nmr spectra of **2a**, **2b**, **3a**, and **3b** were all similar and also showed similar temperature variation, we conclude that the same basic organic ligand is present in all of them. Furthermore, brief reaction of the acetylacetonates **3** with hydrogen chloride regenerated the chloro complexes **2** and suggested that no major structural changes had occurred during the formation of the acetylacetonates.

$$R_2Hg + (PhCN)_2PdCl_2 + MeC{\equiv}CMe \xrightarrow{C_6H_6}$$



2a, R = phenyl
b, R = *p*-tolyl

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Crystal Structure of $\overline{C_5Me_5CH(p\text{-tolyl})CH_2Pd}(acac)$ (3b). The final atomic positional parameters and the isotropic thermal parameters of the atoms are reported in Table I. Interatomic distances are collected in Table II and bond angles in Table III. Figure 1 gives a perspective view of the molecule down the *c** direction onto the *ab* plane; for greater clarity other (but equivalent) representations of the structure are also used in the text.

The unit cell contains two molecules, one each of two optical enantiomers; one is depicted in Figure 1; the other is related to it by a center of inversion. The molecule **3b** basically consists of a 5-substituted penta-

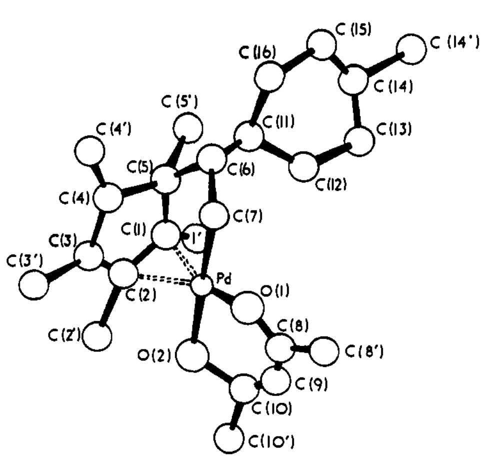

Figure 1. The structure of $[\overline{C_5Me_5CH(p\text{-tolyl})CH_2Pd}(acac)]$ (**3b**).

Table I. Atomic and Thermal Parameters[a]

Atom	*x*	*y*	*z*	*U*, Å^2
Pd	0.04861 (9)	−0.0064 (1)	0.25907 (8)	*b*
O(1)	0.1081 (9)	0.1711 (11)	0.3610 (8)	0.057 (3)
O(2)	0.7680 (9)	0.1381 (11)	0.8883 (7)	0.055 (3)
C(1)	0.0733 (13)	0.1116 (16)	0.8320 (11)	0.045 (4)
C(2)	−0.0281 (14)	0.2541 (17)	0.8302 (12)	0.053 (4)
C(3)	0.0383 (13)	0.2629 (16)	0.7397 (11)	0.048 (4)
C(4)	0.1741 (14)	0.1424 (17)	0.6941 (11)	0.048 (4)
C(5)	0.7822 (12)	−0.0247 (15)	0.2567 (10)	0.041 (4)
C(6)	0.7427 (12)	0.1662 (15)	0.3600 (10)	0.040 (3)
C(7)	0.8730 (13)	0.1505 (16)	0.4022 (11)	0.045 (3)
C(8)	0.2057 (13)	0.1900 (16)	0.3214 (11)	0.047 (4)
C(9)	0.2927 (14)	0.0848 (17)	0.2073 (11)	0.049 (4)
C(10)	0.6942 (13)	0.0711 (11)	0.8867 (11)	0.044 (3)
C(11)	0.6827 (13)	0.3042 (16)	0.3263 (11)	0.044 (3)
C(12)	0.7685 (13)	0.3430 (16)	0.2793 (11)	0.048 (4)
C(13)	0.2941 (14)	0.5277 (18)	0.7487 (12)	0.056 (4)
C(14)	0.4373 (13)	0.4365 (16)	0.7287 (11)	0.049 (4)
C(15)	0.4752 (14)	0.5277 (18)	0.3193 (12)	0.060 (4)
C(16)	0.5359 (13)	0.4019 (16)	0.3491 (11)	0.047 (4)
C(1′)	0.0726 (14)	0.1087 (17)	0.9451 (11)	0.055 (4)
C(2′)	0.8343 (15)	0.4165 (19)	0.9275 (13)	0.068 (4)
C(3′)	−0.0453 (17)	0.3930 (21)	0.7042 (14)	0.082 (5)
C(4′)	0.2835 (16)	0.0914 (20)	0.5880 (13)	0.072 (4)
C(5′)	0.6661 (14)	−0.0344 (17)	0.1977 (12)	0.056 (4)
C(8′)	0.2174 (15)	0.03469 (18)	0.4200 (13)	0.063 (4)
C(10′)	0.5723 (15)	0.1865 (19)	0.0039 (13)	0.069 (4)
C(14′)	0.5054 (17)	0.3008 (21)	0.7637 (14)	0.083 (5)

[a] Estimated standard deviations in parentheses. [b] Anisotropic parameters for Pd in Å^2: U_{11}, 0.0376 (9); U_{22}, 0.0386 (9); U_{33}, 0.0483 (9); U_{12}, −0.0196 (6); U_{13}, −0.0126 (6); U_{23}, 0.0235 (6).

Table II. Bond Lengths for **3b**

Bond	Å	Bond	Å
Pd–O(1)	2.048 (11)	C(2)–C(2′)	1.52 (2)
Pd–O(2)	2.158 (9)	C(3)–C(3′)	1.56 (2)
Pd–C(1)	2.130 (16)	C(4)–C(4′)	1.55 (2)
Pd–C(2)	2.296 (17)	C(5)–C(5′)	1.55 (2)
Pd–C(3)	3.125 (19)	C(11)–C(12)	1.41 (2)
Pd–C(4)	3.47	C(12)–C(13)	1.42 (2)
Pd–C(5)	3.035 (10)	C(13)–C(14)	1.37 (2)
Pd–C(7)	2.025 (12)	C(14)–C(15)	1.41 (2)
C(1)–C(2)	1.39 (2)	C(15)–C(16)	1.40 (2)
C(2)–C(3)	1.47 (2)	C(16)–C(11)	1.40 (2)
C(3)–C(4)	1.31 (2)	C(14)–C(14′)	1.55 (2)
C(4)–C(5)	1.54 (2)	O(1)–C(8)	1.32 (2)
C(5)–C(6)	1.56 (2)	C(8)–C(9)	1.36 (2)
C(5)–C(1)	1.55 (2)	C(9)–C(10)	1.39 (2)
C(6)–C(7)	1.54 (2)	C(10)–O(2)	1.26 (2)
C(6)–C(11)	1.55 (2)	C(8)–C(8′)	1.55 (2)
C(1)–C(1′)	1.54 (2)	C(10)–C(10′)	1.54 (2)

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(9) T. Hosokawa and P. M. Maitlis, *J. Amer. Chem. Soc.*, **95**, 4924 (1973).

Table III. Bond Angles for **3b**[a]

Angle	Deg	Angle	Deg
O(1)-Pd-O(2)	88.6 (4)	C(5)-C(6)-C(11)	113
O(1)-Pd-C(7)	85.3 (5)	C(7)-C(6)-C(11)	114
O(1)-Pd-C(1)	161.2 (4)	C(16)-C(11)-C(12)	118
O(1)-Pd-C(2)	161.1 (5)	C(11)-C(12)-C(13)	120
C(1)-Pd-C(2)	36.3 (6)	C(12)-C(13)-C(14)	121
O(2)-Pd-C(7)	171.8 (6)	C(13)-C(14)-C(15)	120
O(2)-Pd-C(1)	100.9 (4)	C(14)-C(15)-C(16)	119
O(2)-Pd-C(2)	91.4 (5)	C(15)-C(16)-C(11)	122
C(7)-Pd-C(1)	83.5 (5)	C(13)-C(14)-C(14′)	122
C(7)-Pd-C(2)	96.2 (6)	C(15)-C(14)-C(14′)	119
C(5)-C(1)-C(2)	109	C(8)-C(9)-C(10)	127
C(1)-C(2)-C(3)	109	O(1)-C(8)-C(9)	126
C(2)-C(3)-C(4)	110	O(1)-C(8)-C(8′)	113
C(4)-C(5)-C(1)	100	C(9)-C(8)-C(8′)	121
C(1)-C(5)-C(6)	108	O(2)-C(10)-C(9)	128
C(4)-C(5)-C(6)	107	O(2)-C(10)-C(10′)	113
C(5)-C(6)-C(7)	108	C(9)-C(10)-C(10′)	119

[a] Estimated standard deviations for all angles other than those at the metal lie between 1 and 2 deg.

methylcyclopentadiene, one double bond of which [C(1)–C(2)] is coordinated to the metal and the other [C(3)–C(4)] which is free. Two cis coordination sites of the square planar palladium are occupied by the acetylacetonate while the fourth one is σ bonded to CH_2 [C(7)] which is part of a bridge connecting the metal to C(5) of the cyclopentadiene. The three ligand atoms O(1), O(2), and C(7) define a plane which includes the metal and which cuts C(1)–C(2) at an angle of 88°. This intersection is much closer to C(1) (0.4 Å) than to C(2) (1.0 Å).

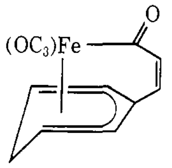
The carbon atoms C(1)–C(5) define a plane (average deviation, 0.014 Å, maximum deviation, 0.021 Å) and the metal projects onto this plane 0.4 Å *outside* the cyclopentadiene ring. The methyl groups C(3′) and C(4′) are slightly (0.14 Å) below the plane, while the methyls attached to the coordinated double bond [C(1′) and C(2′)] are displaced upwards (away from the metal). This distortion is shown more by C(1′) which is 0.67 Å above the plane than by C(2′) which is only 0.50 Å above it. This is again consistent with a greater interaction of the metal and C(1) than with C(2).

The two double bonds are of significantly different lengths, the coordinated one, C(1)–C(2), being as expected[10–12] longer [1.39 (2) Å] than the uncoordinated one, C(3)–C(4) [1.31 (2) Å].

The bridge C(6)–C(7) linking the metal and the cyclopentadiene at C(5) is remarkable only in that all the bond lengths and bond angles are normal for sp^3 carbons and that there is no strain evident here. This situation may be contrasted to that in the complex **4**, which also has a σ- and π-bonded metal in a somewhat analogous arrangement. In this complex the crystal structure determination[14] shows marked angular distortions in the propenoyl bridge between the π-cyclohexadienyl ring and the metal, indicating a considerable strain in the molecule.

The *p*-tolyl group in **3b** is again normal; the isomers present in the crystal have the *p*-tolyl and the coordinated double bond on the same side. In addition, we find that the angle between the normal to the *p*-tolyl plane and the normal to the cyclopentadiene plane is 38°, with C(12) of the *p*-tolyl nearest the metal.

The acetylacetonate is also normal and shows a dihedral angle between the plane containing O(1), C(8), C(9), C(10), and O(2) and that containing O(1), Pd, and O(2) of 11°. However, the two Pd–O distances are *not* equal and differ by 0.11 Å, the longer one, [Pd–O(2)], being trans to the Pd–C(7) bond. This is an example of the high trans influence of a Me–C σ bond in square planar complexes,[15] but it may be noted that the cyclooctenylnickel acetylacetonate, **5**, did *not* show this feature.[16]



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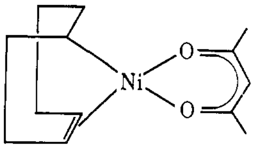

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The palladium–carbon bond lengths are all reasonable; the value of 2.025 (12) Å for Pd–C(7) [sp^3 carbon] compares with that found for a palladium–phenyl bond (sp^2 carbon) of 1.994 (15) Å.[17] The differing lengths of Pd–C(1) and Pd–C(2) show that the metal is closer to C(1) than C(2) and agree with the other data discussed above. The distances of the metal to the other cyclopentadiene carbons are all greater than 3.0 Å and well out of bonding range.

Behavior of $[\overline{C_5Me_5CHRCH_2Pd}X]$ in Solution. The nmr spectra of **2** and **3** all showed variation with temperature, and a typical series of spectra for **3a** in *o*-dichlorobenzene is depicted in Figure 2. The best resolution was achieved for **3a** in *o*-dichlorobenzene but other solvents (CD_2Cl_2, $CHCl_3$, CCl_4, or benzene) gave similar results. Limiting spectra were achieved at temperatures below *ca.* 0° and there was no further change down to −40°; further cooling to −70° resulted in some broadening, probably owing to viscosity effects. Above *ca.* +70° a fairly rapid irreversible rearrangement began to occur (see below).

The limiting low temperature spectrum (−5°, Figure 2) is interpreted in terms of the presence of two isomers in the ratio of 4:1. Since there are only small changes in the spectra on further cooling, it is reasonable to assume that the major isomer is the one present in the crystal, namely **3a**. On this basis, the resonances of **3a** are assigned as follows: δ 0.76 (s, Me_c), 1.62 (s, Me_b), 1.70 (s, Me_b'), 1.79 (s, Me_a), 1.92 (s, Me_a'), 1.82, 1.87 (two singlets, acac methyls), 0.94 (dd, H_δ, $J_{\delta\beta} = 5$ Hz, $J_{\delta\gamma} = 8$ Hz), 2.23 (d, H_γ, $J_{\gamma\beta} = 8$ Hz, $J_{\gamma\beta} \leqslant 1$ Hz), 2.36 (d, H_β, $J_{\beta\delta} = 5$ Hz, $J_{\beta\gamma} \leqslant 1$ Hz).

The methyl on the sp^3 carbon (Me_c) is expected to be at highest field. We have shown that there is a small downfield shift of a vinylic methyl group on coordination to $PdCl_2$ in hexamethyl(Dewar benzene)[18] and,

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(10) E. O. Greaves, C. J. L. Lock, and P. M. Maitlis, *Can. J. Chem.*, **46**, 3879 (1968).

(11) P. M. Maitlis, "The Organic Chemistry of Palladium," Vol. 1, Academic Press, New York, N. Y., 1971, p 113 ff.

(12) See also, for example, the structure of $(Ph_3P)_2Pt$(allene)[13] where the coordinated double bond of the allene [1.48 (5) Å] is again longer than the uncoordinated one [1.31(5) Å].

(13) M. Kadonaga, N. Yasuoka, and N. Kasai, *Chem. Commun.*, 1597 (1971).

(14) P. J. van Vuuren, R. J. Flatterick, J. Meinwald, and R. E. Hughes, *J. Amer. Chem. Soc.*, **93**, 4394 (1971).

(15) Reference 11, pp 37–41 and 88.

(16) O. S. Mills and E. F. Paulus, *Chem. Commun.*, 738 (1966).

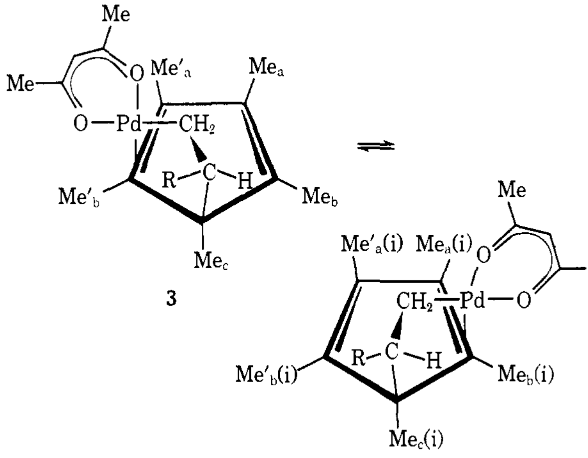
(17) D. L. Weaver, *Inorg. Chem.*, **9**, 2250 (1970).

(18) H. Dietl and P. M. Maitlis, *Chem. Commun.*, 759 (1967).

combined with the generally accepted rule that in pentamethylcyclopentadienes Me_a hydrogens resonate at lower field than Me_b, the assignments given follow. The acetylacetonate methyls (Me) are designated as such since they are of the same shape and height and rather different to the others, as would be expected.

The single hydrogens, H_β, H_γ, and H_δ are assigned on the basis of the benzylic hydrogen, H_β, being at lowest field, and the coupling constants being reasonable for the geometry demanded by the crystal structure of **3b**. The largest coupling is then the geminal one, $J_{\gamma\delta}$. For a dihedral angle between C–H_β and C–H_γ of *ca.* 80° a value for J of 1 Hz or less is reasonable as is a value of 5 Hz for $J_{\beta\delta}$ where the corresponding dihedral angle is about 50°.[19] The position of H_γ is unusual in that it is strongly deshielded.

The remaining resonances, singlets at δ 0.96, 1.10, and 2.05, are the only ones which can be seen of the other isomer; the remainder are presumably hidden under the other methyls of **3a**. We propose this isomer to be **6a**, where the metal is now complexed



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a, R = phenyl; **b**, R = *p*-tolyl

to the other double bond. There is likely to be very little difference in energy between **6a** and **3a** since only the magnitudes of the nonbonded interactions between the phenyl and Me_b' and Me_c are altered. From observations of the mode of coalescence of the resonances on warming up the solution, we assign the resonances as follows: δ 0.96 [Me_c(i)], 1.10 [Me_b'(i)], and 2.06 [Me_b(i)], the resonances arising from isomer **6a** being designated (i).

The chemical shifts for the Me_b methyls in **3a** and **6a** can then be explained if it is assumed that coordination of the double bond shifts Me_b downfield by 0.5 ppm, while the phenyl exerts a shielding effect of *ca.* 0.5 ppm in the opposite direction. In the isomer **6a**, Me_c(i) is at rather higher field than Me_c in **3a** and presumably this must be due to a different orientation of the phenyl group in the two isomers giving different shieldings to the two Me_c methyls.

The exchange process showed a coalescence temperature of +27° for **3a**, and the rates of the process were measured over the temperature range +5 to +25° by the line-width method[20,21] for the coalescence of Me_b and Me_b(i) and Me_b' and Me_b'(i). Owing to the interference of the double doublet of H_δ at δ 0.95, the Me_c resonances could not be used. The rate was unaltered on dilution by a factor of 2 and is therefore a first-order process. The values for $k(Me_b)$ and $k(Me_b')$ obtained are given in Table IV; despite the appreciable scatter owing to the relatively poor spectral data, the values appear reasonable and we have calculated E_a to be 24.5 ± 2.5 kcal mol^{-1} from a least-squares treatment of the data.

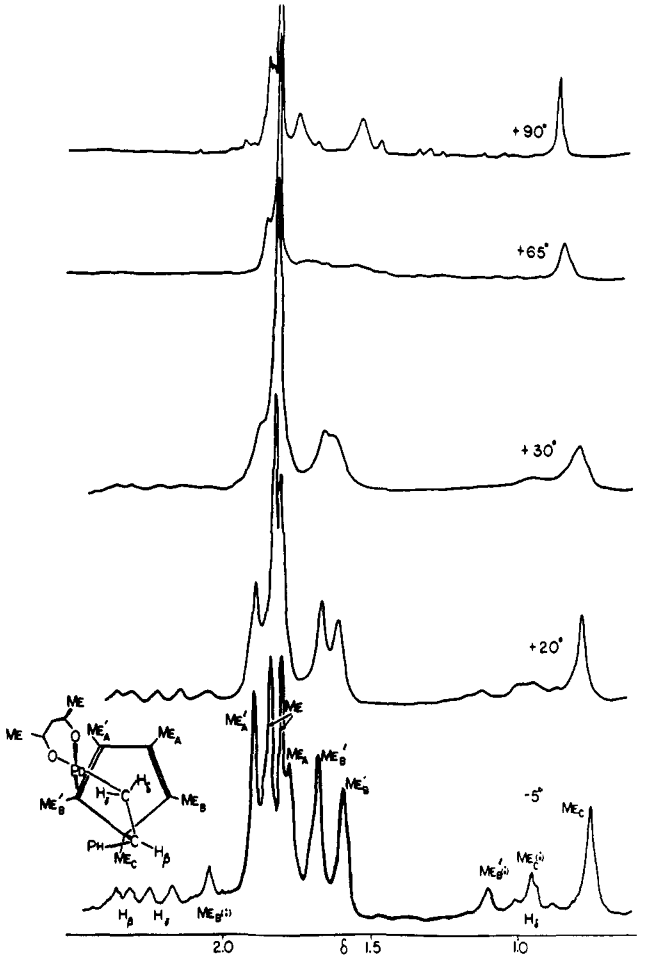

Figure 2. Nmr spectra of $[C_5Me_5CHPhCH_2Pd(acac)]$ (**3a**) (100 MHz in *o*-dichlorobenzene at different temperatures).

Table IV. First-Order Rate Constants for "Flipping" of $[C_5Me_5CHPhCH_2Pd(acac)]$ (**3a**)

Temp, °K	$k(Me_b)$, sec^{-1}	$k(Me_b')$, sec^{-1}
278	1.6	1.6
283	3.9	2.4
285	5.0	3.0
287	10.1	7.9
289	15.0	10.0
291	14.1	15.7
293	17.3	15.7
295.5	23.6	20.4
298	23.0	26.0

Runs in a range of solvents showed the same coalescence temperature and, in particular, addition of dimethyl-d_6 sulfoxide (DMSO-d_6) had no effect on the acetylacetonate **3a**. There is therefore only min-

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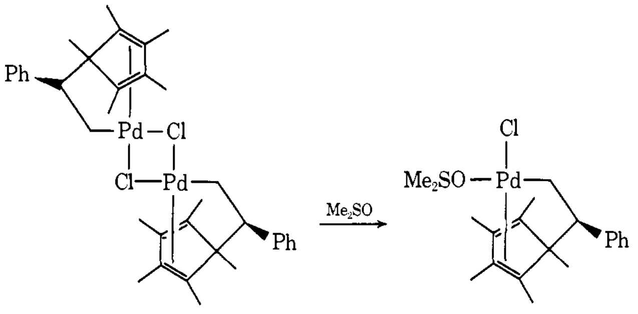
(19) S. Sternhell, *Quart. Rev., Chem. Soc.*, 23, 236 (1969).
(20) G. Binsch, *Top. Stereochem.*, 3, 120 (1968).
(21) C. S. Johnson, *Advan. Magn. Resonance*, 1, 33 (1965).

imal solvent participation in the flipping of the metal from one double bond to the other. This type of stereochemical nonrigidity represents the first example, to our knowledge, of what may be termed "a molecular windshield wiper."

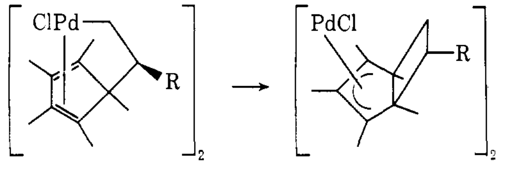
Although the spectra obtained are poorer, the chloride-bridged dimer **2a** shows very similar variation with temperature and approximately the same coalescence temperature. In this case, however, the addition of small amounts of DMSO-d_6 progressively lowers the coalescence temperature and the rate of flipping increases sharply.[22] This effect of DMSO is probably due to its ability to break Pd–Cl bridges to form the monomer 7.



2a **7**

Further studies to elucidate the details of these processes are in progress.

Internal Cyclization of $[C_5Me_5CHRCH_2PdCl]_2$ (3a) to $[(CHRCH_2C_5Me_5)PdCl]_2$ (8a). In addition to the exchange process, the complexes **2a** and **2b** undergo another isomerization reaction. This reaction is very slow at room temperature but is complete in a short time on heating and gives, quantitatively, new complexes, which have been shown to be the bicyclo[3.2.0]hept-2-enyl complexes **8a** and **8b** illustrated, by analysis, molecular weight, spectra, and a degradation reaction.



2 **8**

a, R = phenyl b, R = *p*-tolyl

The nmr spectrum of **8a** showed resonances assigned as follows: δ 0.40 (s, 3 H, $Me_{c'}$), 0.91 (s, 3 H, Me_c), 1.34 (s, 3 H, $Me_{b'}$), 1.37 (s, 3 H, Me_b), 1.97 (s, 3 H, Me_a), 1.98 (m, hidden under Me_a, 1 H, H_β), 3.10 (dd, 1 H, H_γ, $J_{\gamma\beta}$ = 12 Hz , $J_{\gamma\delta}$ = 10 Hz), 4.99 (dd, 1 H, H_δ, $J_{\delta\beta}$ = 8 Hz, $J_{\delta\gamma}$ = 10 Hz), and 7.21 (s, 5 H, phenyl). Similarly, the *p*-tolyl complex **8b** showed resonances at δ 0.44 (s, 3 H, $Me_{c'}$), 0.94 (s, 3 H, Me_c), 1.39 (s, 3 H, $Me_{b'}$), 1.42 (3 H, Me_b), 2.00 (s, 3 H, Me_a), 2.34 (s, 3 H, *p*-tolyl methyl), 2.0 (m, 1 H, hidden under Me_a, H_β), 3.15 (dd, 1 H, H_γ, $J_{\gamma\beta}$ = 12 Hz, $J_{\gamma\delta}$ = 10 Hz), 4.97 (dd, 1 H, H_δ, $J_{\delta\beta}$ = 8 Hz, $J_{\delta\gamma}$ = 10 Hz) and 7.08 (s, 4 H, aromatic hydrogens).

The chemical shifts of the methyl groups are all very reasonable for the structure indicated and $Me_{c'}$ and $Me_{b'}$ in each case show the effect of shielding by the aromatic ring relative to Me_c and Me_b. Me_a is, as usual, the lowest field methyl in **8a**. The coupling constants found for the four-membered ring hydrogens are not unreasonable if one assumes it to be somewhat distorted from planar, with the benzylic carbon bent toward the five-membered ring. In this case the dihedral angle between C–H_β and C–H_γ will be about 150° and a value for J of 12 Hz is very reasonable. The dihedral angle between C–H_β and C–H_δ of around 30° is again consistent with a J of 8 Hz.[19] The reason for the distortion of the cyclobutane probably lies in the nonbonded repulsions between the phenyl (or *p*-tolyl) and $Me_{c'}$; these are minimized if the ring is bent in the manner suggested.

The chemical shifts of H_γ and H_δ are at rather lower fields than might be anticipated for a purely organic compound of similar structure, and we suggest that the low value for H_δ in particular arises from a deshielding effect by the metal and its ligands.[23] This would imply that the palladium is coordinated to the same side of the cyclopentenyl ring as the four-membered ring is fused to and this hypothesis is supported by models which show that the other side of the ring is rather crowded, particularly by Me_c and $Me_{c'}$. For similar reasons the phenyl group must be exo with respect to the metal, and this is consistent with the most probable mode of formation of the complex (see below).

Additional evidence for the structure proposed comes from the far ir spectra which show strong ν_{Pd-Cl} bands at 245 (for **8a**) and 248 cm^{-1} (for **8b**) with shoulders at 252 (**8a**) and 254 (**8b**) cm^{-1}. The observation of two closely spaced peaks argues for a fairly symmetrical Pd_2Cl_2 bridge and is in agreement with a π-allylic structure.[26]

The structure assigned to **8** was also in agreement with the products obtained by the degradation reaction with cyanide and thermally (see below). Reactions of **8a** with potassium cyanide in methanol gave a white inorganic precipitate, presumably $K_2Pd(CN)_4$, and a colorless oil which was shown to contain only one component by vpc and which was identified as an isomer of 1,2,3,4,5-pentamethyl-6(or 7)-phenylbicyclo[3.2.0]hept-2-ene (**9** or **10**).

The nmr spectrum ($CDCl_3$; 100 Hz) was in agreement with this formulation: δ 0.72 (s, 3 H, Me_d), 0.93 (s, 3 H, Me_e), 1.06 (d, 3 H, Me_c, $J(Me_c–H_\epsilon)$ =

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[22] In our preliminary communication[2] we stated, mistakenly, that addition of DMSO-d_6 stopped the flipping entirely because we observed very sharp spectra. In fact, we were observing the *high*-temperature limiting spectrum, not the *low*-temperature one, as subsequent experiments at different temperatures showed. Approximate coalescence temperatures are (molar ratio of DMSO-d_6 to dimer in parentheses): +27° (0:1); +5°; (2:1); −5° (4:1) −30° (from 6:1 to 10:1) in $CDCl_3$ or CH_2Cl_2.

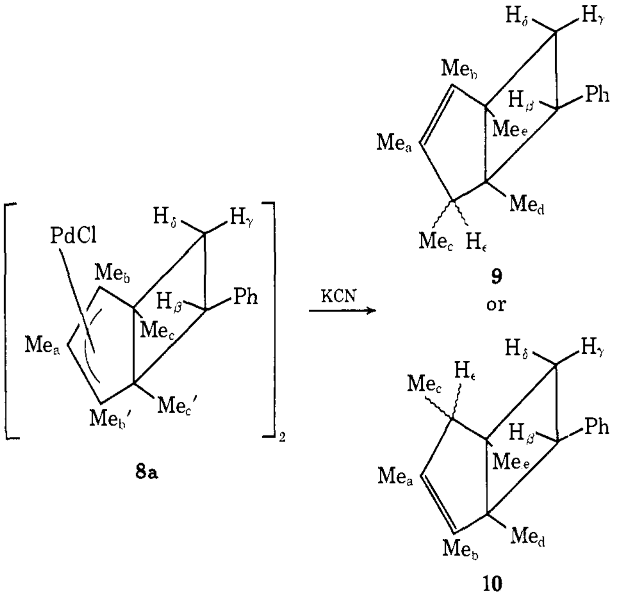
[23] We have observed very similar effects in some related complexes[9] and in a completely unrelated palladium complex.[24] Trofimenko[25] has also made a similar observation in $Ni[Et_2B(pz)_2]_2$. In both the latter cases crystal structure determinations indicate that the hydrogens which are deshielded are those which are situated above the plane of a square planar metal atom and are approximately in the vacant axial coordination site.

[24] D. M. Roe, P. M. Bailey, K. Moseley, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1273 (1972).

[25] S. Trofimenko, *J. Amer. Chem. Soc.*, **89**, 6288 (1967), and personal communication.

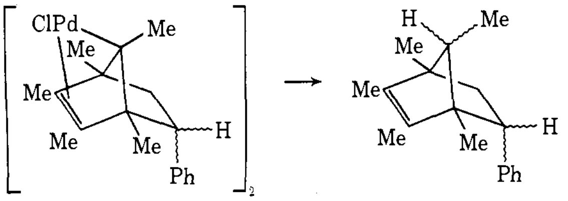
[26] By comparison, ν_{PdCl} for (allyl $PdCl)_2$ are at 243 and 254 cm^{-1}, for $[(2\text{-methylallyl})PdCl]_2$ at 248 and 261 cm^{-1},[27] while the values for the complexes **2a** and **2b** are 235 and 289 cm^{-1} (**2a**) and 227 and 289 cm^{-1} (**2b**); see also ref 4.

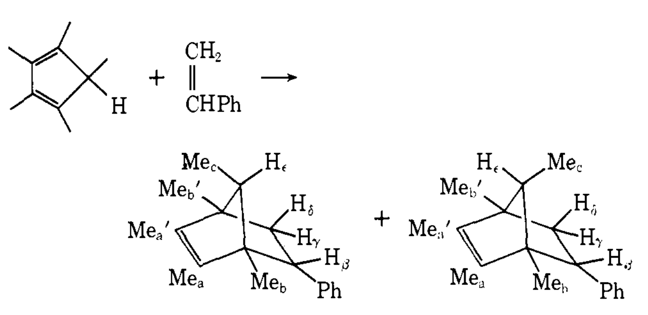
[27] D. M. Adams and A. Squire, *J. Chem. Soc. A*, 1808 (1970).



10.5 Hz), 1.58 (s, 6 H, Me_a and Me_b), 1.95 (d, 1 H, H_γ, $J_{\gamma\delta} = 10.5$ Hz $J_{\gamma\beta} \leqslant 1$ Hz), 1.99 (d, 1 H, H_β, $J_{\beta\delta} = 8.5$ Hz $J(H_\beta\text{–}H_\gamma) \leqslant 1$ Hz), 2.4 (m, 1 H, H_ϵ), 3.37 (dd, 1 H, H_δ, $J_{\delta\beta} = 8.5$ Hz, $J_{\delta\gamma} = 10.5$ Hz), and 7.20 (m, 5 H, phenyl).

An alternative formulation for the hydrocarbon is that of a pentamethyl-5-phenylnorbornene, and this would also require an alternative structure for **8**.





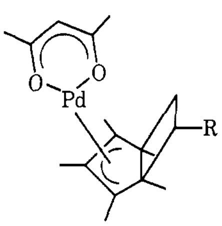
In order to examine this possibility, the Diels–Alder condensation of pentamethylcyclopentadiene and styrene was carried out. This gave (after 6 weeks at 40–45°) two isomeric norbornenes which were separated by vpc and identified as 1,2,3,4-*syn*-7-pentamethyl-5-*endo*-phenylnorbornene (67%) (**11**) and 1,2,3,4-*anti*-7-pentamethyl-5-*endo*-phenylnorbornene (27%) (**12**) by their nmr spectra: **11** ($CDCl_3$, 100 MHz) δ 0.59 (d, 3 H, Me_c, $J(Me_c\text{–}H_\epsilon) = 6$ Hz), 0.92 and 1.09 (ss, 3 H each, Me_b and Me_b'), 0.97 and 1.62 (multiplets, owing to homoallylic coupling, 3 H each, Me_a and Me_a'), 1.40 (q, 1 H, H_ϵ, $J(H_\epsilon\text{–}Me_c) = 6$ Hz), 1.46 (dd, 1 H, H_γ, $J_{\gamma\beta} = 5$ Hz, $J_{\gamma\delta} = 11$ Hz), 1.87 (dd, 1 H, H_δ, $J_{\delta\gamma} = 11$ Hz, $J_{\delta\beta} = 9$ Hz), 2.75 (dd, 1 H, H_β, $J_{\beta\gamma} = 5$ Hz, $J_{\beta\delta} = 9$ Hz), and 7.0 (m, 5 H phenyl); **12** ($CDCl_3$, 100 MHz), δ 0.73 (d, 3 H, Me_c, $J(Me_c\text{–}H_\epsilon) = 7$ Hz), 0.92 and 1.07 (ss, 3 H each, Me_b and Me_b'), 1.02 and 1.70 (multiplets, owing to homoallylic coupling, 3 H each, Me_a and Me_a'), *ca.* 1.55 (m, 1 H, H_γ), 1.92 (m, 1 H, H_δ), 2.92 (dd, broad, 1 H, H_β, $J_{\beta\gamma} = 5$ Hz, $J_{\beta\delta} = 10$ Hz), and 7.0 (m, 5 H, phenyl). In contrast to **11** the resonance of H_γ in **12** is very broad and that owing to H_ϵ could not be clearly distinguished at all. We ascribe this to long-range *W* coupling between these two protons which smears out still further their already split spectra. *W* coupling cannot occur in **11** and the resonances there are much sharper.

A further distinction between **9** (or **10**) and the norbornenes **11** and **12** is in their mass spectra. Those of **11** and **12** are very similar and show the retro-Diels–Alder fragmentation while this type of fragmentation was much less common for **9** (or **10**) which, overall, exhibited a very complex cracking pattern.

It is clear, therefore, that the product from the decomposition of **8** is not a norbornene and this strengthens the structure assignments of both **8** and **9** (or **10**).

The rate of the internal cyclization of **2a** to **8a** was determined by following the changes in nmr spectrum at 36°. The rate was found to be first order in **2a** and to be somewhat solvent dependent: $k_1 = 6.2 \times 10^{-3}$ min^{-1} in $CDCl_3$, 7.1×10^{-3} in benzene, and 1.7×10^{-2} in $CDCl_3$-DMSO-d_6 (1:1).

The acetylacetonates **13** derived from **8** have also been prepared and characterized, as has the presumably ionic *o*-phenanthroline adduct (**14**).



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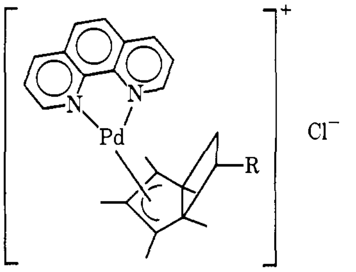


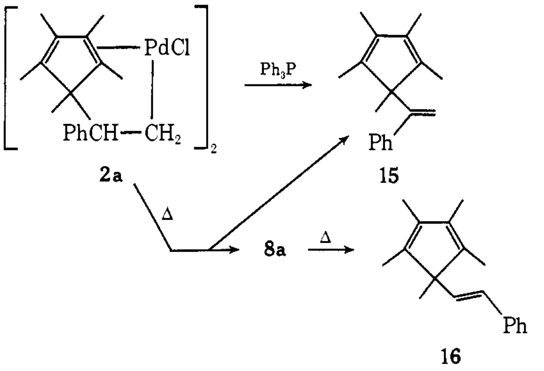
14

Thermal Decomposition of [C_5Me_5-CHPhCH$_2$PdX] (2a and 3a) and [(C_5Me_5-CHPhCH$_2$)PdX] (8a and 13a). Under the influence of a number of reagents such as PPh_3 or *o*-phenanthroline the complex **2a** undergoes β-elimination of "HPdCl" to give α-pentamethylcyclopentadienylstyrene (**15**).[9,28] Thermal decomposition of **2a** also usually gave small quantities of **15** but the major product (*ca.* 69% at 145–150° and 0.4–0.5 mm) was *trans*-β-pentamethylcyclopentadienylstyrene (**16**).[28]

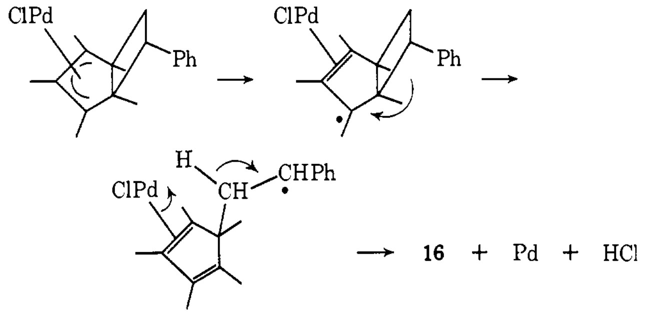
The latter styrene, **16**, was also the major product (84% based on consumed **8a**) from the thermal decomposition of **8a** in benzene (80°, 3 hr), and hence it appeared that **16** was formed from **8a** rather than directly from **2a** in the thermal decomposition of the latter complex. This was confirmed by heating **2a** for 3 hr in benzene at 80°; the products were **16** (10%) and **8a** (87%).

The exact mechanism for decomposition of **8a** to

(28) Nmr of **15** ($CDCl_3$, 100 MHz): δ 1.12 (s, 3 H), 1.64 (m, 12 H, diene methyls in C_5Me_5), 5.17 (d, 1 H, $J(H\text{–}H_{gem}) = 1.5$ Hz), 5.26 (d, 1 H), 7.05 (m, 5 H, phenyl). Nmr of **16** ($CDCl_3$, 60 MHz): δ 1.13 (s, 3 H), 1.70 and 1.81 (multiplets, each 6 H; diene methyls in C_5Me_5), 5.63 (d, 1 H, $J(H\text{–}H_{trans}) = 18$ Hz), 6.51 (d, 1 H), 7.3 (m, 5 H, phenyl).



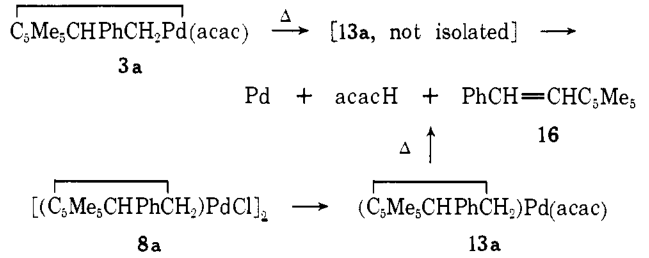
16 is not clear, but a plausible intermediate is a complexed benzylic radical such as **17** which then loses



17

hydrogen from the adjacent carbon. The greater stability of this radical over the one, $C_5MeCHPhCH_2\cdot$, which would be obtained by cleavage of the opposite cyclobutane bond then accounts for the preferential formation of **16**.

Interestingly enough, the acetylacetonate **3a** does not rearrange to the acetylacetonate **13a** on standing at 20°; under these conditions, isomerization of **2a** is complete in about 5 days. On refluxing in benzene for 2.5 hr only **16** and starting material (**3a**) were



$$\underset{\mathbf{3a}}{\overline{C_5Me_5CHPhCH_2Pd}(acac)} \xrightarrow{\Delta} [\mathbf{13a}\text{, not isolated}] \longrightarrow Pd + acacH + \underset{\mathbf{16}}{PhCH{=}CHC_5Me_5}$$

$$\underset{\mathbf{8a}}{[(\overline{C_5Me_5CHPhCH_2})PdCl]_2} \longrightarrow \underset{\mathbf{13a}}{(\overline{C_5Me_5CHPhCH_2})Pd(acac)} \xrightarrow{\Delta} \mathbf{16}$$

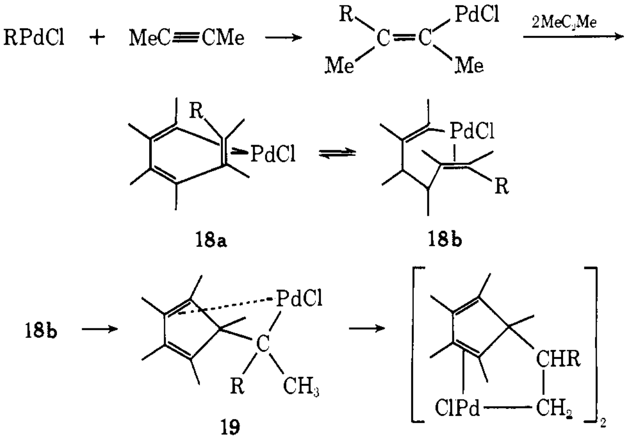
obtained; continued heating for a total of 4.5 hr gave only **16** (74%). In neither case was the acetylacetonate of the bicyclo[3.2.0]heptenyl complex **13a** obtained and this complex could only be prepared from the chloride **8a**.

The acetylacetonate **13a** is therefore less stable than the chloride **8a** and is decomposed faster than it is formed in the decomposition of **3a**. This was confirmed by preparing a sample of **13a** from **8a** and refluxing it in benzene. The decomposition was complete within 2 hr and the products were **16** (76%) and acetylacetone.

Discussion

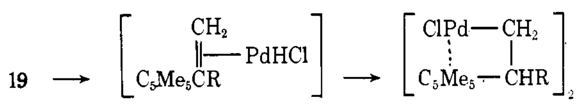
The crystal structure determination of **3b** revealed that it (and therefore also **2a**, **2b**, and **3a**) had a structure in which three butyne molecules had condensed to form a 5-substituted pentamethylcyclopentadiene which was π bonded to two olefinic carbon atoms and σ bonded to the other end of 5 substituent of the ring. Although this structure is quite different to the one we proposed for the product **1**, arising from the direct reaction of $PdCl_2$ and 2-butyne, our work on the latter reaction clearly indicates the close relation between the two processes, since we have shown that **1** very readily undergoes reaction to give 1-substituted-pentamethylcyclopentadienes with a wide variety of reagents.[1] It is furthermore very likely that even the reactions to give hexamethylbenzene proceed through pentamethylcyclopentadiene intermediates. Bearing this in mind, it is therefore very easy to postulate a reasonable mechanism for the formation of **2** from an intermediate **18** analogous to **1** (phenyl or *p*-tolyl in place of Cl). This then implies an analogous mechanism for the formation of **18**. The first step here is the formation (transiently) of "RPdCl" (R = phenyl or *p*-tolyl) which then reacts rapidly with 2-butyne by a series of cis-ligand migrations to give **18**.

$$PdCl_2 + R_2Hg \longrightarrow RPdCl + RHgCl$$



R = phenyl or *p*-tolyl

For reasons not yet fully understood, **18** is not stable and could not be isolated (in contrast to **1**) but underwent an internal cyclization to give **19**. This is also a cis-ligand migration of the vinylic carbon σ bonded to the metal onto the coordinated double bond in **18b**, which is a conformer of **18a** and well arranged for this process. The complex **19** is again not stable, probably because in order for the metal to become coordinatively saturated it must bind to one of the cyclopentadiene double bonds, which is a very unfavorable process involving considerable distortion of the molecule. This strain can be relieved by a 1,2-hydride shift



$$\mathbf{19} \longrightarrow \left[\begin{array}{l} CH_2 \\ \| \!-\!\!-\, PdHCl \\ C_5Me_5CR \end{array}\right] \longrightarrow \left[\begin{array}{l} ClPd\!-\!CH_2 \\ \;\;\vdots \qquad | \\ C_5Me_5\!-\!CHR \end{array}\right]_2$$

which gives **2**. As we have observed, the crystal structure determination shows the complex **2** to be quite strain-free and it therefore obviously corresponds to an energy minimum in the overall process.

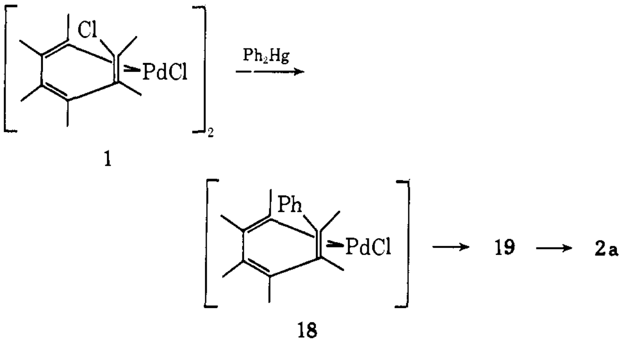
In the formation of **2** no complex **1** and only traces of hexamethylbenzene were observed; this supports our contention that insertion into the Pd–Ph bond is much faster than insertion into Pd–Cl since, if the latter process occurred, substantial amounts of hexamethylbenzene should be formed.

Table V. Analyses

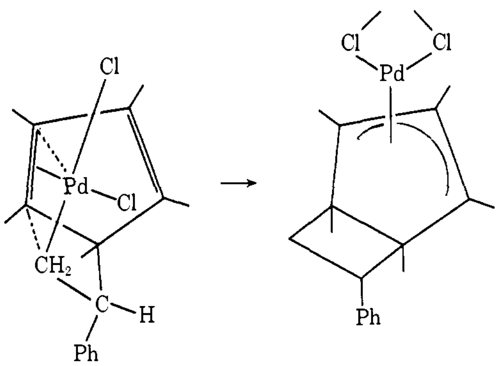
Complex	Calcd C	Calcd H	Calcd Cl	Calcd Other	Found C	Found H	Found Cl	Found Other
$[C_5Me_5CHPhCH_2PdCl]_2$ (**2a**)	56.70	6.08	9.29	Pd, 27.91 Mol wt, 762	56.26	6.30	9.60	Pd, 27.72 Mol wt, 784
$[C_5Me_5CH(p\text{-tolyl})CH_2PdCl]_2$ (**2b**)	57.73	6.37	8.97	Mol wt, 790	57.88	6.28	8.90	Mol wt, 760
$[C_5Me_5CHPhCH_2Pd(acac)]$ (**3a**)	62.09	6.79		Mol wt, 445	62.42	6.75		Mol wt, 411
$[C_5Me_5CH(p\text{-tolyl})CH_2Pd(acac)]$ (**3b**)	62.81	7.03		Mol wt, 458	62.91	7.03		Mol wt, 425
$[C_5Me_5CHPhCH_2Pd(o\text{-phen}]Cl$	64.17	5.56	6.31	N, 4.99	65.13	5.48	6.88	N, 4.42
$[C_5Me_5CHPhCH_2Pd(o\text{-phen})]PF_6$	53.70	4.66		N, 4.17 P, 4.62	55.20	4.56		N, 4.03 P, 4.95
$[C_5Me_5CHPhCH_2Pd(bipy)]PF_6$	51.98	4.84		N, 4.33 P, 4.79	50.36	5.00		N, 4.00 P, 5.20
$[C_5Me_5CHPhCH_2)PdCl]_2$ (**8a**)	56.70	6.08	9.29	Mol wt, 762	56.15	6.17	9.47	Mol wt, 765
$[(C_5Me_5CH(p\text{-tolyl})CH_2)PdCl]_2$ (**8b**)	57.73	6.37	8.97	Mol wt, 790	57.13	6.54	9.39	Mol wt, 760
$[(C_5Me_5CHPhCH_2)Pd(acac)]$ (**13**)	62.09	6.79		Mol wt, 445	62.31	7.35		Mol wt, 438
$[(C_5Me_5CHPhCH_2)Pd(o\text{-phen})]Cl$ (**14**)	64.17	5.56	6.31	N, 4.99	63.09	5.56	6.11	N, 4.70

Somewhat to our surprise though, when the complex **1** was reacted with diphenylmercury *in benzene*, a 57% yield of **2a** was obtained together with some hexamethylbenzene. However, under identical conditions but in *methylene chloride*, **1** reacted with diphenylmercury to give *only* hexamethylbenzene and no **2a** at all. As we have found that **2a** is formed even more conveniently in methylene chloride than in benzene in the direct reaction of butyne, diphenylmercury, and palladium chloride, the processes involved in *this* reaction are different and **1** cannot be an intermediate.

The formation of **2a** from **1** is, notwithstanding this, a very interesting reaction. Heck[8] has reported that phenylation ($PhHgCl + Li_2PdCl_4 + CuCl_2/HOAc$) of vinyl chloride gave stilbene in moderate yields. It therefore appears that vinylic halides when coordinated to Pd(II) will undergo nucleophilic phenylation and Heck's reaction may well be related to the one we observe. If this is the case then we can propose the following mechanism for the formation of **2a** from **1**, where the first product is presumably **18** (R = Ph) and this then rearranges as before to **19** and then **2a**.



The irreversible isomerization of **2** to **8** also appears to be related to the "windshield wiper" rearrangement since similar solvent effects are noted for both; in particular both processes are considerably accelerated in the presence of dimethyl sulfoxide. It is likely that at one stage in both processes the Pd–C σ bond becomes parallel to the coordinated double bond. This is the situation which is most conducive for the occurrence of a cis-ligand migration,[29] and a simple calculation suggests that one irreversible isomerization to **8** occurs for approximately every 10^6 flips of the metal from one double bond to the other.



Experimental Section

Reagents were of AR quality and all reactions were carried out under nitrogen. The light petroleum used was the fraction with bp 30–60°. Analytical data on the complexes are presented in Table V.

Reactions of 2-Butyne with Dichlorobis(benzonitrile)palladium and Diphenylmercury to Give Complex 2a. Dichlorobis(benzonitrile)palladium (1.92 g, 5 mmol) was added slowly in small portions over 15 min to a stirred solution of 2-butyne (2.7 ml, 35 mmol) and diphenylmercury (1.77 g, 5 mmol) in dichloromethane so that the temperature of the solution did not exceed 25°. When about half the palladium complex had been added, a precipitate (identified as phenylmercuric chloride by melting point and ir spectrum) began to appear. After the addition was complete, the solution was stirred for a further 15 min and then light petroleum (50 ml) was added to precipitate PhHgCl (1.08 g). This was filtered off and the bright yellow filtrate was then evaporated to dryness on a rotary evaporator to leave an oily residue. This was shaken up with more light petroleum (125 ml) and the solution filtered to remove the last of the PhHgCl (total yield, 1.42 g). The yellow filtrate was then crystallized at −10° for 18 hr, to give yellow microcrystals of **2a**; yield 0.86 g, 45%. The complex was purified by chromatography in chloroform on a short alumina column and crystallized from light petroleum to give pure **2a**: mp 125–126° dec; $\nu_{C=C}$ 1640 (m) cm^{-1}; nmr of **2a** (220 MHz, $CDCl_3$, −50°) all broad singlets (rel intensities in arbitrary units in brackets) δ 0.86 [0.2], 0.96 [0.15], 1.25 [0.05], 1.70 [0.1], 1.80 [0.25], 1.93 [0.15], 1.99 [0.5], 2.10 [0.07], 2.23 [0.04], 2.29 [0.08], 2.50 [doublet, 0.04], 2.63 [doublet,

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(29) B. L. Shaw, *Chem. Commun.*, 464 (1968).

0.07], 7.27 (doublet), 7.38 (doublet), 7.48 (triplet) [total intensity, 0.42]; at 220 MHz, CDCl$_3$, +37°, broad resonances, δ 0.79–0.98 [0.45], 1.71 and 1.77 [0.35], 1.88 [0.1], 2.01 [0.6], 2.27 [0.1], 2.60 [0.1], 7.34 [0.15], 7.44 [0.2], 8.25 [0.15].

The mother liquor from the initial crystallization was then chromatographed on alumina to give the following fractions.

(i) Elution with light petroleum gave, after removal of solvent, 0.71 g of a colorless oil which was shown to be benzonitrile by ir spectrum and to contain only a trace of hexamethylbenzene (<1%) by nmr.

(ii) Elution with benzene gave a yellow solution which after removal of the solvent and crystallization from light petroleum at −10° gave yellow microcrystals of the tetramer complex "[Ph(C$_2$Me$_2$)$_4$PdCl]$_2$" (0.075 g, 0.17 mmol, 3%), mp 176–177° dec. *Anal.* Calcd for C$_{44}$H$_{50}$Cl$_2$Pd$_2$: C, 60.69; H, 6.71; Cl, 8.14; mol wt 870. Found: C, 60.23; H, 6.95; Cl, 8.95; mol wt 810.

(iii) Finally, elution with chloroform gave a brown solution which, on evaporation, gave a dark brown polymeric solid (0.55 g) with a complex nmr spectrum. This material was not further examined.

[C$_5$Me$_5$CH(*p*-tolyl)CH$_2$PdCl]$_2$ (2b). This was prepared in an identical manner with that described above, from di-*p*-tolylmercury, 2-butyne, and dichlorobis(benzonitrile)palladium: yield of **2b**, 28% (based on Pd); mp 127–129° dec; nmr of **2b** (100 MHz, CDCl$_3$) at −70° δ 0.75–0.96 [0.3], 1.19 [0.02], 1.75 [0.2], 1.88, 1.96 [0.5], 2.26 [0.03], 2.43 [0.15], 2.58 [0.04], 7.08 [0.03], 7.3 [0.1]; and at +37°, broad singlets at δ 0.91 [0.35], 1.77 [0.4], 2.01 [0.5], 2.39 [0.2], 7.2 [0.2], and 8.1 [0.1].

Reaction of [ClC$_6$Me$_6$PdCl]$_2$ (1) with Diphenylmercury. (i) **In Dichloromethane.** Diphenylmercury (0.07 g, 0.02 mmol) was added in small portions over 5 min to a solution of [ClC$_6$Me$_6$PdCl]$_2$ (**1**) (0.07 g, 0.01 mmol) in dichloromethane (3 ml) at 20°. Stirring was continued for a further 5 min after which some insoluble material was filtered off. The solution was then examined by nmr, which showed the presence of only one single peak at δ 2.18, due to hexamethylbenzene. On working up the solution a quantitative yield of hexamethylbenzene was obtained. There was no trace of **2a** in either the final product or the nmr spectrum of the crude material.

(ii) **In Benzene.** A solution of diphenylmercury (0.13 g, 0.04 mmol) and [ClC$_6$Me$_6$PdCl]$_2$ (**1**) (0.13 g, 0.02 mmol) in benzene (20 ml) was stirred for 15 min at 20°. The insoluble material was then filtered off and the solvent removed; examination of the residue by nmr showed that both **2a** and a small amount (*ca.* 5%) of hexamethylbenzene had been formed. The reaction mixture was purified by chromatography on a short alumina column. The hexamethylbenzene was eluted with benzene and the complex **2a** was obtained on elution with chloroform, to give, after crystallization, 0.08 g (51%).

[C$_5$Me$_5$CHPhCH$_2$Pd(acac)] (3a) and [C$_5$Me$_5$CH(*p*-tolyl)CH$_2$Pd(acac)] (3b). The complex **2a** (0.138 g) was dissolved in a solution of potassium acetylacetonate (prepared from 0.085 g of acetylacetone and 0.05 g of potassium hydroxide in 1.5 ml of water) in tetrahydrofuran (20 ml). The solution was stirred at 20° for 30 min and was then evaporated to dryness on a rotary evaporator. The resulting oily material was extracted into light petroleum; this solution was dried (Na$_2$SO$_4$) and filtered, and the solvent was removed to leave a yellow oil which slowly crystallized from methanol to give pale yellow crystals of **3a** (0.125 g, 83%), mp 120–121° dec. The pale yellow *p*-tolyl complex **3b** was prepared in an analogous manner from **2b** in 60% yield, mp 123–124° dec.

The acetylacetonate **3a** was converted into the chloride **2a** and acetylacetone on brief exposure to dry hydrogen chloride. The reaction proceeded essentially quantitatively, as determined by nmr.

X-Ray Crystal Structure Determination of [C$_5$Me$_5$CH(*p*-tolyl)CH$_2$Pd(acac)] (3b). Crystals of **3b** suitable for X-ray studies were obtained by crystallization from methanol–benzene. A crystal, nearly equidimensional, with an average radius of 0.3 mm was selected for data collection. Preliminary precession photographs indicated the crystal to be triclinic. Accurate lattice parameters were determined by least-squares refinement of 15 values of 2θ measured on a four circle Syntex automatic diffractometer. These parameters are: $a = 11.072\ (5)$, $b = 10.034\ (5)$, $c = 13.515\ (5)$ Å; $\alpha = 119.21\ (5)$, $\beta = 88.23\ (5)$, and $\gamma = 63.90\ (5)°$. The calculated density for a cell containing two molecules is 1.353 g/cm^3 compared with a measured value of 1.36 g/cm^3.

Data were collected with the Syntex automatic diffractometer using graphite monochromatized Mo Kα radiation in a θ–2θ mode throughout, and backgrounds were measured at 1° from either side of the peak for a time interval equivalent to that used in the peak scan. Peaks were scanned at a rate varying from 2 to 24° min^{-1} depending on the peak intensity. A standard reflection was measured at intervals of 50 reflections in order to check for changes in either the X-ray source or crystal orientation. A total of 1316 reflections were measured in a hemisphere up to 2θ–35°. The 1147 reflections, after correcting for background, whose peak intensities were greater than 3σ, with σ determined from the counting statistics on the peak and background, were considered observed. Those that yielded apparently negative intensities were left out of the refinement to save on computational expenses. All the reflections were corrected for Lorentz and polarization and absorption effects.

The Pd positions were obtained from three dimensional Patterson functions which indicated that the space group should be $P\bar{1}$. The remainder of the molecule was determined from electron density and difference electron density maps. The structure was refined by full-matrix least-squares, written by J. S. Stephens for the CDC-6400, with individual isotropic thermal parameters on all the atoms except Pd. In the latter case the components of the anisotropic thermal tensor were varied. Weights were determined by the function $w = [5.0 + 0.33F + 0.007F^2]^{-1}$ with the coefficients determined so that $w(|F_o| - |F_c|)^2$, where F_o and F_c are observed and calculated amplitudes of scattering, respectively, would be locally independent of $|F_o|$. The refinement was terminated when the shift over errors, as calculated from the least-squares matrix, was less than 0.25. The final R value, $R = (\Sigma|F_o| - |F_c|)/\Sigma|F_o|$, is 0.055 while the weighted residual, $R_w = (\Sigma w(|F_o| - |F_c|)^2]/\Sigma w|F_o|^2$, is 0.077.

Atomic scattering factors, dispersion corrected, were obtained from ref 30. No attempt was made to either find or refine the hydrogen positions or to refine the anisotropic thermal components of the lighter atoms.[31]

[C$_5$Me$_5$CHPhCH$_2$Pd(*o*-phen)]Cl. *o*-Phenanthroline (0.06 g, 0.33 mmol) was added to a solution of **2a** (0.10 g, 0.14 mmol) in 10 ml of benzene. The solution rapidly precipitated a yellow solid which was filtered off after 15 min; addition of light petroleum to the mother liquor gave more of the same material, total yield 0.14 g, 95%. The analytical sample was crystallized from benzene and light petroleum, mp 169–170° dec; nmr (100 MHz, CDCl$_3$) resonances at δ 1.31, 1.46, 1.57, 1.78, 2.20 (all s, Me's), 1.78, 3.25, 3.58 (all m, 1 H each), 6.75, 7.23, 7.84, 8.30, 9.43 (all m, total 8 H, *o*-phenanthroline).

This complex was converted into the hexafluorophosphate **20**,

[C$_5$Me$_5$CHPhCH$_2$Pd(*o*-phen)]PF$_6$
20

[C$_5$Me$_5$CHPhCH$_2$Pd(bipy)]PF$_6$
21

mp 202° dec, by reaction with ammonium hexafluorophosphate in aqueous tetrahydrofuran. The bipyridyl complex **21**, mp 123° dec, was prepared analogously.

All these complexes decomposed slowly in solution but were reasonably stable as solids at −10°.

Di-μ-chloro-bis(1,2,3,4,5-pentamethyl-7-phenyl-2,3,4-trihaptobicyclo[3.2.0]heptenyl)dipalladium (8a). The complex (**8a**) arises from the isomerization of **2a**, and the reaction was carried out in a number of solvents at various temperatures. In chloroform at 20° 5 days were necessary for completion. A small amount of metal and some impurities were removed by filtering the solution through a short alumina column; the product was crystallized from chloroform–hexane as yellow crystals, yield 68–78%, mp 145–146° dec.

The *p*-tolyl complex (**8b**) was obtained analogously from **2b** in 70% yield as yellow crystals, mp 158–159° dec.

Acetylacetonato(1,2,3,4,5-pentamethyl-7-phenyl-2,3,4-trihaptobicyclo[3.2.0]heptenyl)palladium (13a). This complex was prepared in 78% yield in the identical manner to that used for preparing **3a**: mp 133–135° dec; nmr (100 MHz, CDCl$_3$) δ 0.41 (Me$_c'$), 0.93 (Me$_c$), 1.31 (Me$_b'$), 1.33 (Me$_b$), 2.07 (Me$_a$), 1.90 (acac methyls), 1.96 (dd, H$_\beta$, $J_{\beta\gamma} = 13$ Hz, $J_{\beta\delta} = 8$ Hz), 2.87 (dd, H$_\gamma$, $J_{\gamma\delta} = 10$ Hz), 4.54 (dd, H$_\delta$), 5.16 (s, acac H), 7.24 (m, phenyl).

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(30) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962.

(31) The table of observed and calculated final structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-4914.

o-Phenanthroline(1,2,3,4,5-pentamethyl-7-phenyl-2,3,4-trihaptobicyclo[3.2.0]heptenyl)palladium Chloride (14). *o*-Phenanthroline (0.10 g, 0.57 mmol) was added to a solution of **8a** (0.14 g, 0.18 mmol) in 5 ml of benzene at 20°. A white precipitate immediately formed which was filtered off to give the product **14** (0.19 g, 92%). This was crystallized from benzene–chloroform to give pale yellow crystals of the pure salt: mp 144–145° dec; nmr (100 MHz, $CDCl_3$) δ 0.60, 1.12, 1.82, 1.84, 2.19 (all s, Me's), 2.73 (m, 1 H), 3.71 (m, 1 H), 4.53 (dd, H_δ(?), $J_{\delta\beta}$ = 8 Hz, $J_{\delta\gamma}$ = 10 Hz), 7.10, 7.19, 8.18, 8.36, 8.90, 9.11 (all m, total 8 H, *o*-phenanthroline).

Decomposition of Di-μ-dichloro-bis(1,2,3,4,5-pentamethyl-7-phenyl-2,3,4-trihaptobicyclo[3.2.0]heptenylpalladium) (8a) to 1,2,3,-4,5-Pentamethyl-6 (or 7)-phenylbicyclo[3.2.0]hept-2-ene (9 or 10). Potassium cyanide (0.60 g, 9.2 mmol) was added to a yellow solution of **8a** (0.45 g, 0.59 mmol) in 15 ml of methanol, and the solution was stirred for 18 hr at 20°. A white precipitate (presumably $K_2Pd(CN)_4$) formed rapidly and when the reaction was complete this was filtered off. The solvent was removed from the filtrate to leave an oil (0.08 g, 0.33 mmol, 28%) which on vpc analysis was found to contain largely (94%) one component. This component was purified by preparative vpc (20% SE-30 at 195°) and was shown to be 1,2,3,4,5-pentamethyl-6 (or 7)-phenylbicyclo[3.2.0]hept-2-ene (**9** or **10**). *Anal.* Calcd for $C_{18}H_{24}$: C, 89.93; H, 10.06; mol wt, 240. Found: C, 90.00; H, 9.91; mol wt (mass spectrum), 240.

1,2,3,4,7-Pentamethyl-5-phenylnorbornenes 11 and 12. A solution of pentamethylcyclopentadiene (0.10 g, 0.8 mmol) and styrene (0.09 g, 0.8 mmol) in 0.5 ml of deuteriochloroform was held at 40–45°; the nmr spectrum of the solution was monitored and the changes were followed. When no further changes occurred (after 6 weeks), the solution was chromatographed on alumina (3.2 g). Elution with light petroleum gave a colorless oil (0.134 g) which was analyzed by vpc (20% SE-30 at 175°) and found to contain four components (i–iv). The compounds were separated preparatively and identified. Compounds (iii) and (iv) (about 6% each), which had no phenyl resonances in the nmr and were therefore derived only from pentamethylcyclopentadiene, were not further investigated. The major product, an oil, (i), obtained in 67% yield in 13 min was shown to be 1,2,3,4-*syn*-7-pentamethyl-5-*endo*-phenylnorbornene (**11**). *Anal.* Calcd for $C_{18}H_{24}$: C, 89.93; H, 10.06; mol wt, 240. Found: C, 90.25; H, 10.06; mol wt (mass spectrum), 240.

The product (ii), also an oil, was obtained in 27% yield after 15 min, and was identified as 1,2,3,4-*anti*-7-pentamethyl-5-*endo*-phenylnorbornene (**12**). *Anal.* Calcd for $C_{18}H_{24}$: C, 89.93; H, 10.06; mol wt, 240. Found: C, 89.63; H, 10.32; mol wt (mass spectrum), 240.

Mass Spectra of the Pentamethyl(phenyl)bicycloheptenes. The mass spectral cracking patterns of the three hydrocarbons **9** (or **10**) and **11** and **12** were determined; the two norbornenes showed very similar patterns and only gave significant peaks (rel intensities in parentheses) at *m/e* 240 (1), 239 (1), 152 (12), 137 (29), 136 ($C_5Me_5H^+$, 100), 135 (10), 122 (7), 121 (25), 119 (7), 105 (15), 104 ($PhCHCH_2^+$, 18), 103 (7), 91 (16) for the *syn*-methyl isomer (**11**); 240 (0.5), 239 (0.2), 137 (11), 136 ($C_5Me_5H^+$, 100), 135 (4), 122 (6), 121 (43), 119 (8), 105 (11), 104 ($PhCHCH_2^+$, 28), 103 (10) and 91 (10), for the *anti*-methyl isomer (**12**). In each case the most significant process occurring was the retro-Diels–Alder reaction to pentamethylcyclopentadiene and styrene.

The bicyclo[3.2.0]heptene **9** (or **10**) gave a quite different and much more complex fragmentation at *m/e* 240 (4), 239 (12), 211 (18), 201 (39), 200 (17), 199 (20), 185 (22), 173 (19), 168 (18), 165 (19), 161 (23), 159 (22), 153 (56), 152 (30), 151 (67), 150 (68), 141 (100), 137 (30), 136 (85), 135 (19), 134 (49), 125 (25), 123 (59), 105 (63), 104 (41), 103 (17) and 91 (47). While a retro-Diels–Alder reaction also occurred here, this was not the only fragmentation path and probably not even the most significant one.

In addition, each of the compounds showed significant peaks at *m/e* > 240 arising from recombination reactions.

β-(Pentamethylcyclopentadienyl)styrene (16). A solution of **8a** (0.18 g, 0.24 mmol) in benzene (10 ml) was refluxed for 3 hr. After cooling, the metal was removed by filtration and the filtrate was chromatographed on a short alumina column. Elution with light petroleum gave an oil, identified as β-(pentamethylcyclopentadienyl)styrene (0.03 g), after purification by vpc on a 20% SE-30 column at 185°. *Anal.* Calcd for $C_{18}H_{22}$; C, 90.69; H, 9.30; mol wt, 238. Found: C, 90.81; H, 9.34; mol wt (mass spectrum), 238. Elution of the column with chloroform gave starting material (0.15 g); yield of styrene **16** based on consumed complex **8a** was 84%.

β-(Pentamethylcyclopentadienyl)styrene was also obtained in 59% yield by thermolysis of the complex **2a** in an oil bath at 145–150° at 0.4–0.5 mm (no solvent). In some cases some of the α-(pentamethylcyclopentadienyl)styrene was also obtained.[9] It appears that the exact composition of the product depends critically on the rate of heating. When this reaction was carried out in benzene at 80° for 3 hr a 10% yield of β-(pentamethylcyclopentadienyl)-styrene and a 87% yield of the rearranged complex **8a** were obtained.

On the other hand, when the acetylacetonate **3a** was heated at 80° for 4.5 hr in benzene the only product was β-(pentamethylcyclopentadienyl)styrene (74%) and no **13a** could be detected. When this reaction was examined by nmr after 2.5 hr refluxing only the styrene and the starting complex, **3a**, in the ratio of 60:40, were found.

The acetylacetonate **13a** when refluxed in benzene for 2 hr gave metal, acetylacetone, and β-(pentamethylcyclopentadienyl)styrene (yield, 76%). No starting material was recovered, but a very small amount of a yellow solid which may have been bis(acetylacetonato)-palladium (but which was not further examined) was obtained.

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