Acknowledgment. We thank the Australian Research Council for financial support of this work. We thank Professor W. R. Jackson (Monash University) for a generous gift of the olefin rjo. We are grateful to Drs. E. Horn (**5a,b**), D. Craig (**6**), and W. T. Robinson (**9**) for collection of intensity data for the indicated complexes. M.J.L. was the holder of a Commonwealth Post-Graduate Research Award.

(23) The absolute configurations at ruthenium in **5a,b** can be specified using the Baird–Sloan modifications of the Cahn–Ingold–Prelog priority rules.[24] Thus, the two enantiomers of **5a** in the crystal have *R* and *S* configurations at Ru (*R* illustrated in Figure 1). Spontaneous resolution of **5b** occurred on crystallization, the crystal used for the X-ray study containing only the *R* enantiomer.

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Registry No. 5a, 138630-25-8; **5b**, 138749-87-8; **5c**, 138749-88-9; **6**, 138630-27-0; **9**, 138630-28-1; $C(CN)(CO_2Me)=CH(CO_2Me)$, 54797-29-4; $Ru(C_2Ph)(CO)(PPh_3)(\eta\text{-}C_5H_5)$, 75592-69-7.

Supplementary Material Available: Tables of fractional atomic coordinates, anisotropic thermal parameters, and bond distances and angles for the four structures (14 pages); tables of structure factor amplitudes (59 pages). Ordering information is given on any current masthead page.

Cyclopalladation of *N*-Mesitylbenzylideneamines. Aromatic versus Aliphatic C–H Activation

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The action of $Pd(AcO)_2$ on the imines $2,4,6\text{-}(CH_3)_3C_6H_2CH{=}N(CH_2)_n\text{-}2'\text{-}RC_6H_4$ (R = H, *n* = 0–2 (**1a–c**); R = CH_3, *n* = 1 (**1d**)), in refluxing acetic acid, affords six-membered endo metallacycles possessing an aliphatic carbon–metal bond, in preference to four-, five-, or six-membered exo metallacycles with an aromatic carbon–metal bond. The five-membered exo metallacycles can be obtained by working under milder conditions and isomerize to the more stable six-membered endo metallacycles in refluxing acetic acid. The action of $Pd(AcO)_2$ on the imines $2\text{-}CH_3\text{-}3\text{-}R^1\text{-}4\text{-}R^2C_6H_2CH{=}NC_6H_5$ (R^1 = H, R^2 = CH_3 (**1f**); R^1 = CH_3, R^2 = CH_3O (**1g**)) affords the five-membered endo metallacycles with an aromatic carbon–metal bond, but with the imine $2,5\text{-}(CH_3)_2C_6H_3CH{=}NC_6H_5$ (**1e**) the methyl group at carbon 5 prevents the metalation of the ortho carbon atom and the endo six-membered metallacycle with an aliphatic carbon–metal bond is formed. The reasons for the preference to form endo compounds and the high stability of six-membered derivatives containing Pd–C benzylic bonds are discussed.

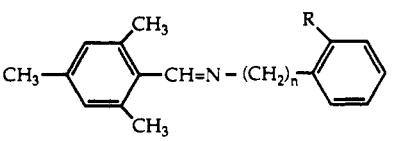
Introduction

The question of aromatic versus aliphatic C–H bond activation has aroused considerable interest over the last few years. In intermolecular processes where an oxidative addition of C–H bonds occurs, it has been observed that there are many more examples of aromatic than aliphatic or benzylic C–H activations. Although the benzylic and alkylic C–H bonds are weaker than the aromatic ones, the greater bond strength of the $M\text{–}C_{aryl}$ over the $M\text{–}C_{alkyl}$ or $M\text{–}C_{benzyl}$ bonds has been proposed as the explanation.[1]

It is generally accepted that there may be substantial similarities between intermolecular and intramolecular activations of C–H bonds; thus, the study of cyclometalation reactions may give valuable insight into intermolecular C–H activations.[2]

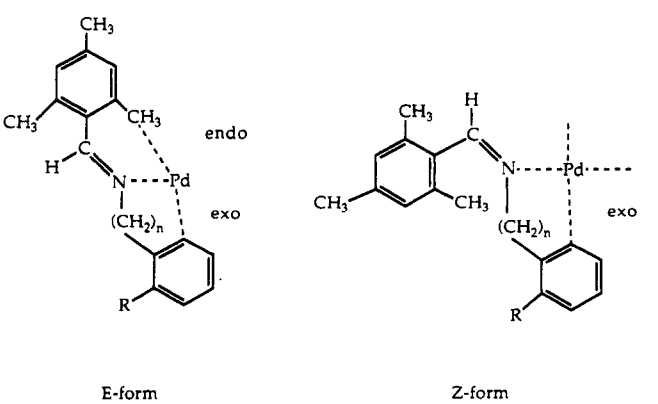
Cyclopalladation reactions of N-donor ligands have been extensively studied, but the factors that control the process are not thoroughly understood. In general, an intramolecular electrophilic attack of the metal at the carbon atom, a strong tendency to form five-membered rings, and preferential activation of aromatic over aliphatic C–H bonds are widely accepted.[3] Although electrophilic dissociation of C–H bonds is not as severely limited as is oxidative addition by thermodynamic constraints associated with the weakness of M–H and M–C bonds and, for example, the stabilization of the leaving group H^+ is important in the thermodynamic driving force of the process,

Chart I



1a (n=0, R=H)
1b (n=1, R=H)
1c (n=2, R=H)
1d (n=1, R=CH_3)

Chart II



E-form Z-form

(1) (a) Hill, C. L. *Activation and Functionalization of Alkanes*; Wiley: New York, 1989. (b) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91. (c) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *107*, 620. (d) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (e) Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41.

(2) (a) Lavin, M.; Holt, E. M.; Crabtree, R. H. *Organometallics* **1989**, *8*, 99. (b) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403.

(3) (a) Brice, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *10*, 73. (b) Omae, I. *Chem. Rev.* **1979**, *79*, 287. (c) Newkome, G. R.; Puckett, W. E.; Gupta, V. K.; Kiefer, G. E. *Chem. Rev.* **1986**, *86*, 451. (d) Omae, I. *Coord. Chem. Rev.* **1988**, *83*, 137. (e) Dunina, V. V.; Zalevskaya, O. A.; Potatov, V. M. *Russ. Chem. Rev.* **1988**, *57*, 250.

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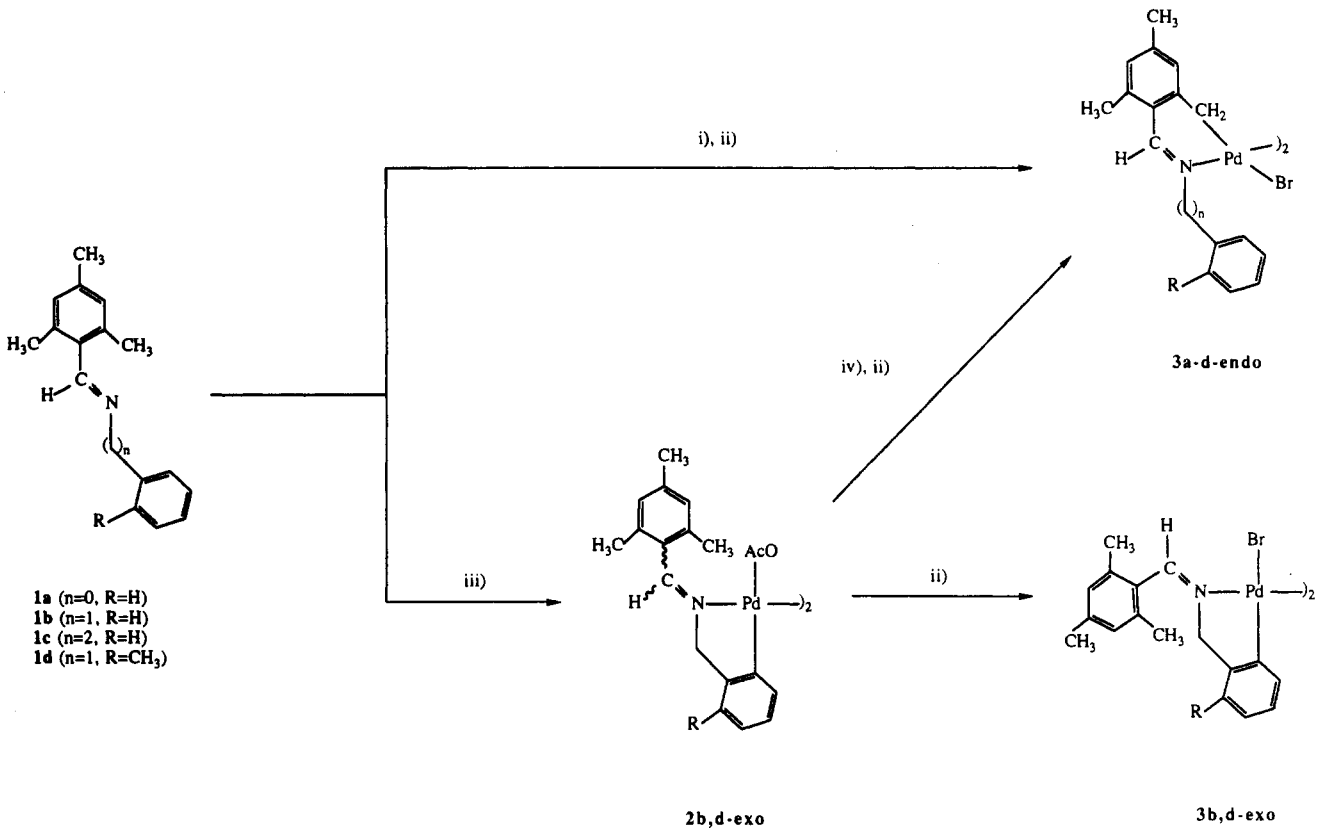
Scheme I[a]



[a] Legend: (i) $Pd(AcO)_2$, HAcO, reflux, 45 min; (ii) LiBr, EtOH; (iii) $Pd(AcO)_2$, HAcO, 60 °C for **1b** or 40 °C for **1d**, 2 h (see text); (iv) HAcO, reflux, 45 min.

M–H and M–C bond strengths still play an important role in the interpretation of the cyclometalation reaction.

In order to obtain more information on the factors that influence the ease and mode of cyclometalation reactions, especially the nature of the carbon atom involved, we report here the cyclopalladation of *N*-benzylideneamines **1a–d** (Chart I). From these ligands, endo and exo metallacycles can be obtained according to the carbon atom metalated. The formation of one type or another depends on the isomeric form adopted by the ligand; i.e., from the *E* form, endo and exo cyclometalated derivatives can be obtained, but from the *Z* isomer only exo compounds can be formed (Chart II). These ligands also allow simultaneous comparison of the metalation tendency of aromatic or aliphatic carbon atoms and the importance of the size of the cycle formed. Thus, the metalation of the *o*-methyl groups should give six-membered endo compounds containing $Pd–C_{benzyl}$ bonds, while the metalation of the aromatic carbon atoms would give exo-cyclometalated derivatives with four-, five-, or six-membered rings for n = 0–2, respectively. The metalation of the methyl substituent of the benzylic ring in **1d**, which could give a six-membered exo metallacycle, is not expected.

A preliminary account of part of this work has been published.[4]

Results

The action of $Pd(AcO)_2$ on the imines **1a–d** in refluxing acetic acid for 45 min and subsequent treatment of the residue obtained with LiBr in ethanol afford the bromo-bridged derivatives **3a–d**-*endo* (Scheme I). Under these experimental conditions, the metalation of one *o*-methyl substituent is achieved with formation of six-membered endo derivatives. These results are especially remarkable for imines **1b** and **1d**, where n = 1, since the metalation of the aromatic carbon atom should give five-membered derivatives containing $Pd–C_{aromatic}$ bonds.

The five-membered exo metallacycles can be obtained by working under milder conditions. Thus, when the imine and $Pd(AcO)_2$ are stirred for 2 h in acetic acid, at 60 °C for **1b** or 40 °C for **1d**, a solution containing both the five-membered exo and the six-membered endo derivatives (in the proportion 2:1) is formed. The addition of ether to the residue formed by evaporation of acetic acid and cooling to −25 °C for 2 days produces the precipitation as major compounds of the exo-acetato-bridged complexes **2b,d**-*exo*. The corresponding bromo-bridged compounds **3b,d**-*exo* are easily obtained by reaction with LiBr in ethanol. Analogous results are found by reaction in toluene at room temperature for 48 h.

Refluxing the exo-acetato-bridged compounds **2b,d**-*exo* in acetic acid (45 min) and subsequent by treating the residues obtained with LiBr in ethanol afford quantitatively the thermodynamically stable six-membered endo derivatives **3b,d**-*endo*. However, in refluxing toluene, no change is observed in the palladated carbon atom, showing that the break of the Pd–C bond only occurs in acid media.

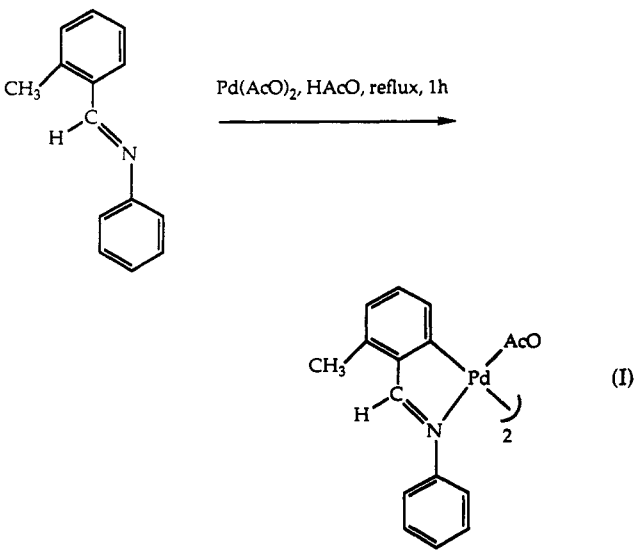
The conversion of **2b,d**-*exo* to **3b,d**-*endo* can be seen as an example of an intramolecular exchange reaction. Ryabov[5] has reported a similar reaction with the amine 1-(3,4-dimethoxyphenyl)-2-methyl-3-(4-nitrophenyl)-2-azopropane $(3,4\text{-}(MeO)_2C_6H_3CH_2N(CH_3)CH_2C_6H_4\text{-}4'\text{-}NO_2)$ and $Pd(AcO)_2$. In chloroform, in which $Pd(AcO)_2$ exhibits

(4) Albert, J.; Granell, J.; Sales, J.; Solans, X.; Font, M. *Organometallics* **1986**, *5*, 2567.

(5) Ryabov, A. D. *Inorg. Chem.* **1987**, *26*, 1252.

electrophilic properties, cyclometalation takes place at the dimethoxy-substituted ring, while in acetic acid the nitro-substituted ring is metalated. Moreover, if the initial solution obtained in chloroform is heated in acetic acid, the latter compound is formed. The driving force of the isomerization process is determined by the different resistance of the two metallacycles toward acidolysis: Pd(II) will migrate to the ligand that forms the palladacycle less susceptible to acidolysis. In our case the thermodynamically stable metallacycles contain a Pd–C_{benzyl} bond, which is weaker than one Pd–$C_{aromatic}$ bond; then the driving force of the reaction can be attributed to the endo structure of the metallacycles that contain the imine C=N bond. The initial formation of the exo-cyclometalated derivatives is a consequence of the rapid electrophilic attack of the Pd(II) at the ortho aromatic carbon atom.

It is known[6] that the action of $Pd(AcO)_2$ on *N*-(2-methylbenzylidene)aniline in refluxing acetic acid for 1 h gives only the five-membered endo derivative with a Pd–$C_{aromatic}$ bond (eq I). Not even under drastic experimental



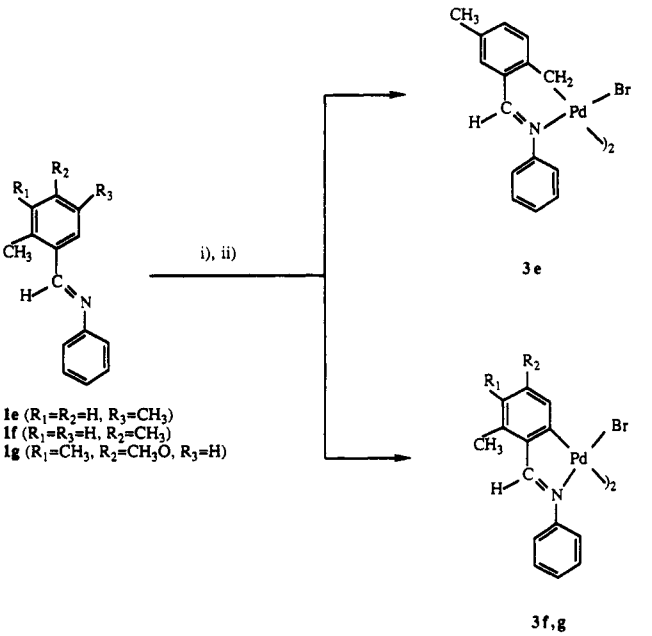
(I)

conditions such as a long time of reaction (24 h) or treatment with $Pd(CF_3COO)_2$ in trifluoroacetic acid is the activation of the C–H aliphatic bond achieved.

We have extended this study to other analogous *N*-benzylideneamines containing methyl substituents in the benzyl ring (Scheme II). With *N*-(2,5-dimethylbenzylidene)aniline (**1e**), the metalation of the *o*-methyl substituent takes place with formation of the six-membered endo derivative **3e**. However, with the other imines studied, **1f** and **1g**, only the five-membered endo metallacycles containing Pd–$C_{aromatic}$ bonds **3f** and **3g** are obtained. These different results can be explained by steric effects in the cyclometalated complexes formed. Thus, in *N*-(2,5-dimethylbenzylidene)aniline (**1e**), the metalation of the ortho carbon atom is prevented by the methyl group at carbon 5, and metalation of the other methyl substituent takes place, with the formation of the endo six-membered derivative. In the other cases, metalation of the ortho carbon atoms occurs, with the formation of five-membered endo-cyclometalated compounds.

To obtain more soluble mononuclear compounds, the action of an excess of phosphines on the cyclometalated complexes **3** has been studied. Compounds with one phosphine, [$\overline{Pd(C\text{-}N)Br(PR_3)}$] (R = Ph, **4**; R = Et, **5**), or complexes with two phosphines, *trans*-[Pd(C-N)Br(PR_3)$_2$]

Scheme II[a]



[a] Legend: (i) $Pd(AcO)_2$, HAcO, reflux, 45 min; (ii) LiBr, EtOH.

(R = Ph, **6**; R = Et, **7**), where the Pd–N bond has been broken, can be obtained.

The stability of the Pd–N bond in cyclometalated derivatives of *N*-benzylideneamines is in general very dependent on the basicity of the nitrogen atom. Thus, while the action of PPh_3 on *N*-benzylideneaniline derivatives gives complexes without Pd–N bonds,[7] from *N*-benzylidenebenzylamine derivatives, with a more basic nitrogen atom, only cyclometalated complexes are formed.[8] With the more basic phosphine PEt_3, both types of imine derivatives give the complexes in which the Pd–N bond has been broken.

Additions of an excess PPh_3 on five-membered endo-cyclometalated complexes derived from aniline, **3f** and **3g**, give the compounds *trans*-[Pd(C-N)Br(PPh_3)$_2$] (**6f,g**) (^{31}P NMR data: 29.07 (s) and 29.12 (s) ppm, respectively). Chromatography of these compounds on a SiO_2 column, with chloroform/methanol as the eluent, affords the cyclometalated compounds [$\overline{Pd(C\text{-}N)Br(PPh_3)}$] (**4f,g**). These results can be accounted for in terms of an intramolecular attack of nitrogen atom to form the cyclometalated compound, as has been previously proposed.[9] A similar mechanism was proposed to account for the ^1H NMR spectra of metalated azobenzenes.[10] Exo metallacycles derived from benzylamines **3b**-*exo* and **3d**-*exo* give only the cyclometalated compounds **4**, in contrast with the analogous exo-cyclometalated complexes of *N*-(2,6-dichlorobenzylidene)amines, where the Pd–N bond is broken under these conditions.[11] The mesityl substituent probably increases the basicity of the nitrogen atom. With the more basic and smaller PEt_3, the compounds *trans*-[Pd(C-N)Br(PEt_3)$_2$] (**7b,d**) are obtained. Six-membered endo-cyclometalated complexes containing Pd–C_{benzyl}

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bonds give only the cyclometalated complexes [Pd(C-N)Br(PR_3)] (**4** with PPh_3 or **5** with PEt_3), even with the aniline derivatives **3a,e**.

Proton NMR spectra (Experimental Section) afford conclusive evidence of the palladated position. In compounds **4**, aromatic protons of the palladated aromatic ring in five-membered metallacycles and those of the palladated benzylic unit in six-membered metallacycles appear shifted to high field. This effect could be caused by a phosphine phenyl ring, suggesting a cis arrangement of the phosphine and the metalated carbon atom and, consequently, a trans arrangement between phosphorus and nitrogen atoms. The ^{31}P chemical shifts of these compounds, 41–43 ppm in five-membered derivatives and 36–37 ppm in six-membered complexes, agree with this trans arrangement.[11]

The chemical shift of methinic protons is a useful tool for the structural characterization of cyclopalladated complexes. This signal appears shifted to high field (0.3–1.3 ppm) relative to that of the free imine in the endo derivatives.[7,8] In the exo metallacycles the imine ligand can adopt the *E* or the *Z* form. In compounds with the imine in the *Z* form, the iminic hydrogen is low-field-shifted relative to the corresponding free ligand. This downfield shift can be explained by the paramagnetic anisotropy of the metal,[12] showing a close vicinity between Pd and H atoms according to the *Z* form adopted by the coordinated imine.[11] In the exo compounds with the imine in the *E* form, this proton appears very near to the position in the free ligand, showing that the proton is not under the paramagnetic influence of the metal.[9] In all the exo compounds obtained in this work the iminic proton is downfield-shifted, showing that the imine is in the *Z* form, except for the acetato-bridged compounds **2b**-*exo* and **2d**-*exo*. Nevertheless, in these cases, due to the open-book shape adopted by the acetato-bridged compounds, it is not possible to establish unambiguously the form adopted by the imine. In compounds **7** with two PEt_3 ligands, the imine is in the *E* form, analogous to the results found in the *N*-(2,6-dichlorobenzylidene)amine derivatives.[11]

The ^{13}C NMR spectra of some six-membered endocyclometalated derivatives containing Pd–C_{benzyl} bonds are summarized in the Experimental Section. The metalated carbon atom (Pd–CH_2–) is shifted downfield by ~10 ppm in the PPh_3-containing complexes **4** and only ~4 ppm in complexes **5** with PEt_3. The signals for the other carbon atoms, including the methinic carbon, do not move. In analogous cyclopalladated complexes the metalated aromatic carbon atoms undergo larger downfield shifts, ~30 ppm.[7b,13]

Discussion

It is well-known that N-donor ligands have a strong tendency to give five-membered cyclopalladated compounds containing Pd–$C_{aromatic}$ bonds. For example, in the series of amines of the type $Ph(CH_2)_nNMe_2$ (n = 0–3) only benzylamine (n = 1) is cyclopalladated;[14] other amines form only coordination compounds.

In systems where there is a possibility of choice between several modes of metalation, five-membered compounds are, as a rule, obtained.[15] In the cyclopalladation of 1-(arylazo)naphthalenes, four metallacycles can be formed, as a result of the presence of two nitrogen donor atoms and three aromatic rings suitable for metalation. Only after the complete blocking by methyl groups of the ortho carbon atoms is it possible to achieve the palladation of the peri carbon atom of the naphthyl group, with formation of a six-membered ring. Even so, five- or six-membered metallacycles with Pd–C sp^3 bonds would have resulted by metalation of the methyl groups.[15c]

Few six-membered cyclopalladated compounds containing Pd–$C_{aliphatic}$ bonds have been reported. Thus, the compound $[Pd(CH_2CMe_2CH_2C_5H_4N)(AcO)]_2$ has been obtained from 2-neopentylpyridine and $Pd(AcO)_2$.[16] Mesitylbenzalazines can also be metalated, giving six-membered metallacycles containing Pd–$C_{aliphatic}$ bonds,[17] but in any case the formation of five-membered rings with these ligands is possible.

It is also known that *N*-benzylideneamines have a strong tendency to give endo derivatives.[8,11] The only exo metallacycles of imines obtained by C–H activation are derivatives of N-2,6-(dichlorobenzylidene)amines, which contain chloro substituents on the ortho positions of the benzal ring.[11] Recently exo- and also endo-cyclopalladated derivatives of *N*-benzylidenebenzylamines have been obtained by oxidative addition of the corresponding *o*-bromoimines on Pd(0) complexes.[9,18]

The results described in this work confirm the strong tendency of imines to form endocyclic compounds. This tendency (endo effect) is so strong that it permits the activation of an aliphatic C–H bond with formation of a six-membered ring in preference to the activation of an aromatic C–H bond with formation of a five-membered ring.

It is generally accepted that the sequence of metal–carbon bond energies M–Ph > M–vinyl > M–CH_3 > M–CH_2R > M–CHR_2 M–CR_3 > M–CH_2Ph and also the easier metalation of the aromatic C–H bonds than the aliphatic C–H bonds show that the product bond strengths (M–C) dominate the position of the hydrocarbon activation equilibria, not the reactant (C–H) bond strengths.[1b]

Unfortunately, the bond energies of Pd–C bonds are not known, but it seems reasonable that the difference between Pd–Ph and Pd–CH_2Ph should be similar to what has been found for rhodium compounds. Since a value of 16–17 kcal/mol[1b] has been proposed for the difference in energy between Rh–Ph and Rh–CH_2R bonds, it is possible to suppose that the stability produced by an endo structure is, at least, of this order.[19]

There is not a clear explanation for the greater stability of the endocyclic compounds. Electronic and steric–structural effects can be important in explaining this effect. Crociani et al.[20] have proposed the formation of a five-membered aromatic ring, involving the two conjugated bonds C=C and N=N, and the filled palladium d orbitals of appropriate symmetry to explain the IR spectra of

(12) Miller, R. G.; Stauffer, R. D.; Fahey, D. R.; Parnell, D. R. *J. Am. Chem. Soc.* **1970**, *92*, 1511.
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(14) Cope, A. C.; Friedrich, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 909.
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(18) Clark, P. W.; Dyke, S. F.; Smith, G.; Kennard, C. H. L. *J. Organomet. Chem.* **1987**, *330*, 427.
(19) It should be noted that the conclusions about thermodynamics that can be drawn from comparisons between different systems are not rigorous. Thus, for example, the effect of changing the metal in a particular transition-metal complex is less well understood than the effect which arises from changing the ligand. Other effects such as changing the coordination geometry around the metal by using rigid ligands, or by using very bulky ligands, also affect the bond strengths in the molecule. Unfortunately, these effects are presently difficult to quantify.
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Table I. Bond Distances (in Å) and Bond Angles (in deg) of Cyclometalated Complexes of *N*-Benzylideneamines

compd	Pd—C	Pd—N	C=N	∠CPdN	∠PdNC	ref
[Pd(acac)(C_6H_4CH=$NCH_2C_6H_5$)] (I)	1.955 (7)	2.008 (5)	1.28 (1)	81.4 (3)	115.2 (5)	18
[Pd(acac)($C_6H_4CH_2N$=CHC_6H_5)] (II)	1.955 (9)	2.034 (9)	1.28 (1)	81.0 (4)	112.3 (8)	18
[Pd{1-CH_2-2-(CH=NC_6H_5)-3,5-$(CH_3)_2C_6H_2$}BrPPh_3] (III)	2.060 (5)	2.138 (4)	1.275 (8)	82.2 (2)	118.3 (4)	4
[Pd{2-{$(CH_2)_2N$=CH(2′,6′-$Cl_2C_6H_3$)}-5-$CH_3OC_6H_3$}BrPPh_3] (IV)	2.002 (3)	2.124 (3)	1.280 (4)	84.5 (1)	119.0 (2)	11

metalated azobenzenes. However, the C=N bond lengths of exocyclic and endocyclic five-membered cyclopalladated derivatives of *N*-benzylidenebenzylamines[18] are identical and, in consequence, the existence of such aromatic rings in endocyclic imine derivatives does not seem very probable.

Table I shows structural data for some cyclometalated derivatives. Compound I is a five-membered endo complex with a Pd–$C_{aromatic}$ bond, and II is a five-membered exo compound also with a Pd–$C_{aromatic}$ bond. Compound III is a six-membered endo complex with a Pd–$C_{aliphatic}$ bond; the metallacycle has a half-skew chair conformation with the palladium atom −1.235 Å out of the plane. Compound IV is a six-membered exo derivative with a Pd–$C_{aromatic}$ bond, and the cycle has a boat conformation with palladium (−1.032 Å) and one methylenic carbon (−0.708 Å) atom out of the plane defined by the remaining four atoms. The values of bond distances and bond angles are not very different; the slight differences observed can be explained by the carbon atom radii or by the trans influence of the other ligands. It is especially remarkable that the iminic bond distances C=N are practically equal in the compounds compared. Thus, it is not easy to relate the stability of these cyclometalated compounds on the basis of their structural features; probably the difference in energy between the two types of metallacycles is not large enough to be reflected in the structural parameters.

The different ring strains of endocyclic and exocyclic compounds could also explain the different stabilities of such compounds, but, unfortunately, the evaluation of this strain is not easy.

In conclusion, these studies have proved that the size of the metallacycle is not the decisive factor in the cyclopalladation of imines. Other more subtle factors, as in this case the endo effect, can be important enough to decide the position where the metalation takes place. Therefore, the supposition that five-membered cyclometalated compounds are the most stable because the ring size would have the most ideal geometry of all the possible ring size[3d] is not of general application. Besides, the assumption that metal ions preferring a square-planar geometry favor five-membered rings is also unnecessarily limiting.

Experimental Section

Routine NMR spectra were obtained on a Bruker WP 80 SY (^{1}H, 80.13 MHz; ^{31}P{^{1}H}, 32.8 MHz; ^{13}C{^{1}H}, 50.3 MHz) spectrometer; 200- and 500-MHz ^{1}H NMR spectra were obtained on Varian XL-200 and XL-500 spectrometers. Chemical shifts (in ppm) were measured relative to $SiMe_4$ for ^{1}H and ^{13}C and relative to 85% H_3PO_4 for ^{31}P. The solvents used were $CDCl_3$ in ^{1}H and ^{13}C and $CHCl_3$ in ^{31}P measurements. Microanalyses were performed by the Institut de Química Bio-Orgànica de Barcelona (CSIC).

Materials and Syntheses. Solvents were dried and distilled before use. Imines were preparated according to published methods.[21]

[Pd(1-CH_2-2-{CH=N$(CH_2)_n$(2′-RC_6H_4)}-3,5-$(CH_3)_2C_6H_2$Br]$_2$ (*n* = 0, R = H (3a-*endo*); *n* = 1, R = H (3b-*endo*); *n* = 2, R = H (3c-*endo*); *n* = 1, R = CH_3 (3d-*endo*)). A stirred suspension of $Pd(AcO)_2$ (0.5 g, 2.2 mmol) in anhydrous acetic acid (30 mL) was treated with an excess of imine **1a**, **1b**, **1c**, or **1d** (4.4 mmol) and the mixture refluxed for 45 min. The solution was filtered to eliminate a small amount of black palladium formed. The filtrate was concentrated in vacuo, and the resulting residue was dissolved in ethanol (20 mL) and treated with LiBr (0.38 g, 4.4 mmol). Compounds **3a–d**-*endo* were precipitated as orange or yellow powders in 70–90% yield. Characterization data are as follows. **3a**-*endo*: ^{1}H NMR (80 MHz) 8.01 s (2 H), 7.66–7.60 and 7.37–7.25 br m (10 H), 6.99 s (2 H), 6.81 s (2 H), 3.26 s (4 H), 2.37 s (6 H), 2.26 s (6 H). Anal. Calcd (found) for $C_{32}H_{32}N_2Br_2Pd_2$: C, 47.0 (46.4); H, 3.9 (3.9); N, 3.4 (3.2). **3b**-*endo*: ^{1}H NMR (80 MHz) 7.92 s (2 H), 7.57–7.54 and 7.37–7.25 br m (10 H), 7.00 s (2 H), 6.70 s (2 H), 5.10 s (4 H), 3.07 s (4 H), 2.29 s (6 H), 2.25 s (6 H). Anal. Calcd (found) for $C_{34}H_{36}N_2Br_2Pd_2$: C, 48.3 (48.1); H, 4.2 (4.2); N, 3.3 (3.3). **3c**-*endo*: ^{1}H NMR (80 MHz) 7.68 s (2 H), 7.31–7.20 br m (10 H), 7.01 s (2 H), 6.37 s (2 H), 4.16 br t (4 H), 3.55 br t (4 H), 3.17 s (4 H), 2.21 br s (12 H). Anal. Calcd (found) for $C_{36}H_{40}N_2Br_2Pd_2$: C, 49.5 (49.5); H, 4.6 (4.5); N, 3.2 (3.2). **3d**-*endo*: ^{1}H NMR (80 MHz) 7.60 s (2 H), 7.25–7.21 br m (8 H), 7.00 s (2 H), 6.73 s (2 H), 5.16 s (4 H), 3.19 s (4 H), 2.35 s (6 H), 2.25 s (6 H), 2.11 s (6 H). Anal. Calcd (found) for $C_{36}H_{40}N_2Br_2Pd_2$: C, 49.5 (49.7); H, 4.6 (4.8); N, 3.2 (3.1).

[Pd(2-{CH_2N=CH-2′,4′,6′-$(CH_3)_3C_6H_2$}-3-RC_6H_3)AcO]$_2$ (R = H (2b-*exo*), R = CH_3 (2d-*exo*)). A stirred suspension of $Pd(AcO)_2$ (0.5 g, 2.2 mmol) in acetic acid (40 mL) was treated with 2.2 mmol of imine **1b** or **1d** at 60 or 40 °C for 2 h, respectively. The solution was concentrated in vacuo and diethyl ether (10 mL) added; cooling at −25 °C for 48 h produces the precipitation as major compounds of **2b,d**-*exo* which are obtained pure in 20% yield after purification by SiO_2 column chromatography with chloroform–methanol (100/2) as eluent. Characterization data are as follows. **2b**-*exo*: ^{1}H NMR (500 MHz) 8.54 s (2 H), 6.95–6.60 br m (12 H), 4.15 AB quartet (4 H), 2.24 s (6 H), 2.15 s (12 H), 2.09 s (3 H), 1.60 s (3 H). Anal. Calcd (found) for $C_{38}H_{42}N_2O_4Pd_2$: C, 56.8 (56.6); H, 5.3 (5.2); N, 3.5 (3.5). **2d**-*exo*: ^{1}H NMR (200 MHz) 8.54 s (2 H), 6.85–6.66 br m (10 H), 3.80 AB quartet (4 H), 2.25 s (6 H), 2.15 s (12 H), 2.07 (6 H), 1.84 s (3 H), 1.69 s (3 H). Anal. Calcd (found) for $C_{40}H_{42}N_2O_4Pd_2$: C, 58.0 (57.8); H, 5.1 (5.0); N, 3.4 (3.2).

[Pd(2-{CH_2N=CH-2′,4′,6′-$(CH_3)_3C_6H_2$}-3-RC_6H_3)Br]$_2$ (R = H (3b-*exo*), R = CH_3 (3d-*exo*)). A stirred suspension of 0.5 mmol of compounds **2b,d**-*exo* in ethanol (20 mL) was treated with 1 mmol of LiBr (0.087 g) at room temperature for 30 min. Compounds **3b,d**-*exo* were precipitated as yellow solids in 70–90% yield. Characterization data are as follows. **3b**-*exo*: ^{1}H NMR (80 MHz) 9.13 br s (2 H), 7.49–7.47 and 7.00–6.80 br m (12 H), 4.61 br s (4 H), 2.31 s (6 H), 2.19 s (12 H). Anal. Calcd (found) for $C_{34}H_{36}N_2Br_2Pd_2$: C, 48.3 (48.6); H, 4.3 (4.3); N, 3.3 (3.2). **3d**-*exo*: ^{1}H NMR (200 MHz) 9.07 br s (2 H), 7.40 br d (2 H), 6.92 s (4 H), 6.79 br t (4 H), 4.54 br s (4 H), 2.32 s (6 H), 2.20 s (12 H), 2.01 s (6 H). Anal. Calcd (found) for $C_{36}H_{40}N_2Br_2Pd_2$: C, 49.5 (49.4); H, 4.6 (4.6); N, 3.2 (3.1).

Conversion of 2b,d-*exo* to 3b,d-*endo*. A suspension of 0.5 mmol of compounds **2b,d**-*exo* in acetic acid (40 mL) was refluxed for 45 min. The solution was concentrated in vacuo, and the residue was dissolved in ethanol (10 mL) and treated with 1 mmol of LiBr (0.087 g) at room temperature for 30 min. Compounds **3b,d**-*endo* were precipitated in quantitative yield.

[Pd(1-CH_2-2-{CH=NC_6H_5}-4-$CH_3C_6H_3$)Br]$_2$ (3e) and [Pd(2-{CH=NC_6H_5}-3-CH_3-4-R^1-5-R^2C_6H)Br]$_2$ (R^1 = H, R^2 = CH_3 (3f), R^1 = CH_3, R^2 = CH_3O (3g)). A stirred suspension of $Pd(AcO)_2$ (0.5 g, 2.2 mmol) in acetic acid (30 mL) was treated with an excess of imine **1e**, **1f**, or **1g** (4.4 mmol) and refluxed for 45

(21) Bigelow, L. A.; Eatough, H. In *Organic Syntheses*; Blatt, A. H. Ed.; Wiley: New York, 1944; Vol. 1, p 80.

min. The solution was filtered to eliminate a small amount of black palladium formed. The filtrate was concentrated in vacuo, and the residue was dissolved in ethanol and treated with an excess of LiBr (0.382 g, 4.4 mmol). The solids obtained were purified by column chromatography over SiO_2 with chloroform as eluent. Compounds **3e**, **3f**, and **3g** were obtained in 60–80% yield. Characterization data are as follows. **3e**: ^{1}H NMR (80 MHz) 7.76 s (2 H), 7.36–7.24 br m (16 H), 3.35 s (4 H), 2.19 s (6 H). Anal. Calcd (found) for $C_{30}H_{28}N_2Br_2Pd_2$: C, 45.7 (45.5); H, 3.6 (3.5); N, 3.5 (3.4). **3f**: ^{1}H NMR (80 MHz) 8.13 br s (2 H), 7.5–7.3 br m (12 H), 6.62 br s (2 H), 2.40 s (6 H), 1.70 s (6 H). Anal. Calcd (found) for $C_{30}H_{28}N_2Br_2Pd_2$: C, 45.7 (45.7); H, 3.6 (3.6); N, 3.5 (3.5). **3g**: ^{1}H NMR (80 MHz) 8.12 br s (2 H), 7.35 br m (12 H), 3.80 s (6 H), 2.35 s (6 H), 2.03 s (6 H). Anal. Calcd (found) for $C_{32}H_{32}N_2O_2Br_2Pd_2$: C, 45.2 (44.6); H, 3.8 (3.7); N, 3.3 (3.2).

[Pd(1-CH_2-2-{CH=N(CH_2)$_n$(2′-RC_6H_4)}-3,5-$(CH_3)_2C_6H_2$)-BrPPh_3] (*n* = 0, R = H (4a-*endo*); *n* = 1, R = H (4b-*endo*); *n* = 2, R = H (4c-*endo*); *n* = 1, R = CH_3 (4d-*endo*)), [Pd-(2-{CH_2N=CH-2′,4′,6′-$(CH_3)_3C_6H_2$}-3-RC_6H_3BrPPh_3] (R = H (4b-*exo*), R = CH_3 (4d-*exo*)), [Pd(1-CH_2-2-{CH=NC_6H_5}-4-$CH_3C_6H_3$)BrPPh_3] (4e), and [Pd(2-{CH=NC_6H_5}-3-CH_3-4-R^1-5-R^2C_6H)BrPPh_3] (R^1 = H, R^2 = CH_3 (4f); R^1 = CH_3, R^2 = CH_3O (4g)). A stirred suspension of 0.25 mmol of compounds **3** in acetone (20 mL) was treated with an excess of PPh_3 (0.262 g, 1 mmol) at room temperature for 30 min. The solutions formed were concentrated in vacuo, and the residues of the reactions were dissolved in diethyl ether (10 mL). The solids obtained, compounds **4a–d**-*endo*, **4b,d**-*exo*, and **4e** (which contain one PPh_3 molecule per palladium atom) and **6f,g** (which contain two PPh_3 molecules per palladium atom), were purified by SiO_2 column chromatography with chloroform or chloroform–methanol (100/1) as eluent. Compounds **4** were obtained in 60–80% yield. Characterization data are as follows. **4a**-*endo*: ^{1}H NMR (80 MHz) 8.20 d ($^4J_{PH}$ = 12 Hz) (1 H), 7.77–7.24 br m (20 H), 6.66 s (1 H), 5.60 (s, 1 H), 2.87 d ($^3J_{PH}$ = 5 Hz) (2 H), 2.36 s (3 H), 2.05 s (3 H); ^{13}C NMR 160.73 (CH=N), 30.21 (CH_2—Pd), 21.18 (CH_3), 18.92 (CH_3); ^{31}P NMR 37.12 s. Anal. Calcd (found) for $C_{34}H_{31}NBrPPd$: C, 60.9 (60.2); H, 4.6 (4.8); N, 2.1 (1.9). **4b**-*endo*: ^{1}H NMR (80 MHz) 8.18 d ($^4J_{PH}$ = 13 Hz, 1 H), 7.84–7.25 br m (20 H), 6.66 s (1 H), 5.60 br s (3 H), 2.35 d ($^3J_{PH}$ = 5 Hz, 2 H), 2.32 s (3 H), 2.03 s (3 H); ^{13}C NMR 159.17 (CH=N), 66.99 (CH_2), 29.60 (CH_2—Pd), 21.13 (CH_3), 18.84 (CH_3); ^{31}P NMR 37.43 s. Anal. Calcd (found) for $C_{35}H_{33}NBrPPd$: C, 61.4 (61.3); H, 4.8 (5.0); N, 2.0 (2.0). **4c**-*endo*: ^{1}H NMR (80 MHz) 7.99–7.25 br m (21 H), 6.61 s (1 H), 5.60 s (1 H), 4.64 br t (2 H), 3.42 t ($^3J_{HH}$ = 7 Hz) (2 H), 2.53 d ($^3J_{PH}$ = 5 Hz) (2 H), 2.24 s (3 H), 2.03 s (3 H); ^{13}C NMR 159.78 (CH=N), 64.74 (CH_2), 37.24 (CH_2), 30.01 (CH_2—Pd), 21.06 (CH_3), 18.72 (CH_3); ^{31}P NMR 36.42 s. Anal. Calcd (found) for $C_{36}H_{35}NBrPPd$: C, 61.9 (61.6); H, 5.0 (5.0); N, 2.0 (2.1). **4d**-*endo*: ^{1}H NMR (80 MHz) 7.85–7.25 br m (20 H), 6.63 s (1 H), 5.52 br s (3 H), 2.47 s (3 H), 2.44 d ($^3J_{PH}$ = 4 Hz, 2 H), 2.23 s (3 H), 2.02 s (3 H); ^{13}C NMR 159.52 (CH=N), 64.23 (CH_2), 29.67 (CH_2—Pd), 21.16 (CH_3), 19.77 (CH_3), 18.78 (CH_3); ^{31}P NMR 37.20 s. Anal. Calcd (found) for $C_{36}H_{35}NBrPPd$: C, 61.9 (61.6); H, 5.0 (5.2); N, 2.0 (1.8). **4b**-*exo*: ^{1}H NMR (500 MHz) 9.66–9.65 m (1 H), 7.74–7.70 and 7.40–7.29 br m (15 H), 6.84 s (2 H), 6.80 d ($^3J_{HH}$ = 6 Hz) (1 H), 6.74 t ($^3J_{HH}$ = 6 Hz) (1 H), 6.36–6.29 m (2 H), 4.71 br s (2 H), 2.25 s (3 H), 2.13 s (6 H); ^{31}P NMR 41.81 s. Anal. Calcd (found) for $C_{35}H_{33}NBrPPd$: C, 61.4 (60.4); H, 4.8 (4.8); N, 2.0 (1.9). **4d**-*exo*: ^{1}H NMR (500 MHz) 9.73 m (1 H), 7.44–7.29 br m (15 H), 6.84 s (2 H), 6.57 m (1 H), 6.23 m (2 H), 4.64 br s (2 H), 2.25 s (3 H), 2.13 s (6 H), 1.97 s (3 H); ^{31}P NMR 42.09 s. Anal. Calcd (found) for $C_{36}H_{35}NBrPPd$: C, 61.9 (61.5); H, 5.0 (5.0); N, 2.0 (2.0). **4e**: ^{1}H NMR (80 MHz) 7.99 d ($^4J_{PH}$ = 12 Hz, 1 H), 7.85–7.15 br m (20 H), 7.09 s (1 H), 6.82 d ($^3J_{HH}$ = 7 Hz) (1 H), 6.02 d ($^3J_{HH}$ = 7 Hz) (1 H), 2.97 d ($^3J_{PH}$ = 4 Hz) (2 H), 2.23 s (3 H); ^{31}P NMR 37.50 s. Anal. Calcd (found) for $C_{33}H_{29}NBrPPd$: C, 60.3 (58.9); H, 4.4 (4.3); N, 2.1 (1.9). **4f**: ^{1}H NMR (80 MHz) 8.43 d ($^4J_{PH}$ = 7 Hz) (1 H), 7.71–7.20 br m (20 H), 6.45 s (1 H), 6.02 br d (1 H), 2.38 s (3 H), 1.61 s (3 H); ^{31}P NMR 42.41 s. Anal. Calcd (found) for $C_{33}H_{29}NBrPPd$: C, 60.3 (59.4); H, 4.4 (4.5); N, 2.1 (2.0). **4g**: ^{1}H NMR (80 MHz) 8.49 d ($^4J_{PH}$ = 7 Hz, 1 H), 7.75 and 7.37–7.24 br m (20 H), 5.92 d ($^4J_{PH}$ = 7 Hz, 1 H), 2.78 s (3 H), 2.38 s (3 H), 1.92 s (3 H); ^{31}P NMR 43.89 s. Anal. Calcd (found) for $C_{34}H_{31}NOBrPPd$: C, 59.4 (58.4); H, 4.5 (4.3); N, 2.0 (1.8).

[Pd(1-CH_2-2-{CH=N(CH_2)$_n$(2′-RC_6H_4)}-3,5-$(CH_3)_2C_6H_2$)-BrPEt_3] (*n* = 0, R = H (5a-*endo*); *n* = 1, R = H (5b-*endo*); *n* = 2, R = H (5c-*endo*); *n* = 1, R=CH_3 (5d-*endo*)). A stirred suspension of 0.25 mmol of compounds **3a–d**-*endo* in acetone (20 mL) was treated with an excess of PEt_3 (1 mmol) at room temperature under nitrogen for 30 min. The solutions formed were concentrated in vacuo, and the residue of the reactions was dissolved in ethanol (10 mL). The solids obtained were purified by SiO_2 column chromatography with chloroform or chloroform–methanol (100/1) as eluent. Compounds **5a–d**-*endo* were obtained in 60–80% yield. Characterization data are as follows. **5a**-*endo*: ^{1}H NMR (80 MHz) 8.22 d ($^4J_{PH}$ = 12 Hz, 1 H), 7.62–7.24 br m (5 H), 6.73 s (1 H), 6.28 s (1 H), 2.98 d ($^3J_{PH}$ = 4 Hz) (2 H), 2.38 s (3 H), 2.26 s (3 H), 2.01–1.71 and 1.38–0.93 br m (15 H); ^{13}C NMR 160.79 (CH=N), 24.59 (CH_2—Pd), 21.45 (CH_3), 18.97 (CH_3), 16.58 d ($^1J_{PC}$ = 28 Hz) (CH_2), 8.36 s (CH_3); ^{31}P NMR 27.97 s. Anal. Calcd (found) for $C_{22}H_{31}NBrPPd$: C, 50.2 (50.3); H, 5.9 (5.9); N, 2.7 (2.6). **5b**-*endo*: ^{1}H NMR (80 MHz) 8.16 d ($^4J_{PH}$ = 12 Hz) (1 H), 8.08–7.25 br m (5 H), 6.70 br s (2 H), 5.38 br s (2 H), 2.53 d ($^3J_{PH}$ = 4 Hz) (2 H), 2.32 s (3 H), 2.22 s (3 H), 2.01–1.72 and 1.34–1.14 br m (15 H); ^{13}C NMR 159.45 (CH=N), 66.47 (CH_2), 24.18 (CH_2—Pd), 21.31 (CH_3), 18.79 (CH_3), 16.33 d ($^1J_{PC}$ = 29 Hz) (CH_2), 8.13 s (CH_3); ^{31}P NMR 26.97 s. Anal. Calcd (found) for $C_{23}H_{33}NBrPPd$: C, 51.1 (51.2); H, 6.1 (6.2), N, 2.6 (2.6). **5c**-*endo*: ^{1}H NMR (80 MHz) 7.90 d ($^4J_{PH}$ = 11 Hz) (1 H), 7.25 br m (5 H), 6.75 s (1 H), 6.66 s (1 H), 4.51–4.39 br m (2 H), 3.41 t ($^3J_{HH}$ = 7 Hz) (2 H), 2.66 d ($^3J_{PH}$ = 5 Hz) (2 H), 2.23 br s (6 H), 2.01–1.72 and 1.34–1.14 br m (15 H); ^{13}C NMR 159.54 (CH=N), 64.78 (CH_2), 37.02 (CH_2), 24.46 (CH_2—Pd), 21.20 (CH_3), 18.65 (CH_3), 16.40 d ($^1J_{PC}$ = 29 Hz) (CH_2), 8.27 s (CH_3); ^{31}P NMR 26.50 s. Anal. Calcd (found) for $C_{24}H_{35}NBrPPd$: C, 51.9 (52.0); H, 6.3 (6.3); N, 2.5 (2.6). **5d**-*endo*: ^{1}H NMR (80 MHz) 7.78 d ($^4J_{PH}$ = 11 Hz) (1 H), 7.46 and 7.13 br m (4 H), 6.76 s (1 H), 6.68 s (1 H), 5.49 br s (2 H), 2.71 d ($^3J_{PH}$ = 5 Hz) (2 H), 2.43 s (3 H), 2.21 br s (6 H), 2.05–1.65 and 1.25–0.87 br m (15 H); ^{13}C NMR 159.69 (CH=N), 63.65 (CH_2), 24.41 (CH_2—Pd), 21.37 (CH_3), 19.69 (CH_3), 18.73 (CH_3), 16.42 d ($^1J_{PC}$ = 29 Hz) (CH_2), 8.26 s (CH_3); ^{31}P NMR 26.59 s. Anal. Calcd (found) for $C_{24}H_{35}NBrPPd$: C, 51.9 (51.6); H, 6.3 (6.5); N, 2.5 (2.3).

***trans*-[Pd(2-{CH_2N=CH-2′,4′,6′-$(CH_3)_3C_6H_2$}-3-RC_6H_3)Br-(PEt_3)$_2$] (R = H (7b), R = CH_3 (7d)).** A stirred suspension of 0.25 mmol of compounds **3b,d**-*exo* in acetone (20 mL) was treated with an excess of PEt_3 (1 mmol) at room temperature under nitrogen for 30 min. The solutions formed were concentrated in vacuo and the residues of the reactions dissolved in ethanol (10 mL). The solids obtained were recrystallized from dichloromethane–methanol (1/1). Compounds **7b,d** were obtained in 60–80% yield. Characterization data are as follows. **7b**: ^{1}H NMR (80 MHz) 8.75 s (1 H), 7.25 and 6.87 br m (4 H), 5.00 s (2 H), 2.43 s (6 H), 2.27 s (3 H), 1.53 and 1.24–1.05 br m (30 H); ^{31}P NMR 12.37 s. Anal. Calcd (found) for $C_{29}H_{48}NBrP_2Pd$: C, 52.8 (51.9); H, 7.3 (7.2); N, 2.1 (2.1). **5d**: ^{1}H NMR (80 MHz) 8.84 s (1 H), 7.25–7.23 and 6.87–6.45 br m (5 H), 5.22 s (2 H), 2.40 s (6 H), 2.27 s (3 H), 2.20 s (3 H), 1.53 and 1.21–1.02 br m (30 H); ^{31}P NMR 12.01 s. Anal. Calcd (found) for $C_{30}H_{50}NBrP_2Pd$: C, 53.6 (53.4); H, 7.5 (7.5); N, 21. (2.1).

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Registry No. **1a**, 34143-85-6; **1b**, 105205-91-2; **1c**, 105205-92-3; **1d**, 138753-46-5; **1e**, 138753-47-6; **1f**, 138753-48-7; **1g**, 138753-49-8; **2b**-*exo*, 138753-50-1; **2d**-*exo*, 138753-51-2; **3a**-*endo*, 127849-34-7; **3b**-*endo*, 138753-52-3; **3b**-*exo*, 123977-98-0; **3c**-*endo*, 138753-53-4; **3d**-*endo*, 138753-54-5; **3d**-*exo*, 123977-99-1; **3e**, 138753-55-6; **3f**, 138753-56-7; **3g**, 138753-57-8; **4a**-*endo*, 105205-93-4; **4b**-*endo*, 105205-94-5; **4b**-*exo*, 138753-59-0; **4c**-*endo*, 105205-95-6; **4d**-*endo*, 138753-58-9; **4d**-*exo*, 138753-60-3; **4e**, 138753-61-4; **4f**, 138753-62-5; **4g**, 138753-63-6; **5a**-*endo*, 138753-65-8; **5b**-*endo*, 138753-66-9; **5c**-*endo*, 138753-67-0; **5d**-*endo*, 138753-68-1; **6f**, 138753-64-7; **6g**, 138783-21-8; **7b**, 138753-69-2; **7d**, 138753-70-5.