

A Detailed Study of (η^3 -Cyclohexenyl)palladium Systems

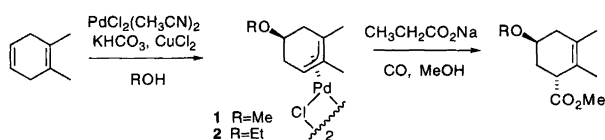
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Martin, J. T., Oslob, J. D., Åkermark, B. and Norrby, P.-O., 1995. A Detailed Study of (η^3 -Cyclohexenyl)palladium Systems. – Acta Chem. Scand. 49: 888–893 © Acta Chemica Scandinavica 1995.

The primary products from palladium(II)-assisted nucleophilic addition to 1,4-cyclohexadienes (η^3 -cyclohexenyl)palladium complexes) have been investigated by NMR spectroscopy. The chloride-bridged dimers are shown to interconvert rapidly between diastereomeric form with exchange of monomeric units. The boat–chair equilibrium is too fast to be frozen out even at -130°C . An anomalous *cis* addition product is shown to be formed indirectly from the normal *trans* product.

It has long been recognized that several palladium-catalyzed functionalizations of unsaturated substrates proceed via (η^3 -allyl)palladium intermediates. Included in the range of reactions available are functionalizations of cyclohexenes, 1,3-cyclohexadienes, and 1,4-cyclohexadienes,¹ as well as acyclic 1,4- to 1,7-dienes.² Under stoichiometric conditions, the intermediate (η^3 -allyl)palladium complexes can often be isolated and studied.³ The final product distribution is affected by conformational equilibria and reactivity differences in the (η^3 -allyl)palladium complexes. Despite extensive work (for a discussion, see, e.g., Ref. 7) selectivity control is difficult in these reactions. This is especially true if chiral induction is the goal.^{4,5} The final, selectivity-determining step is frequently nucleophilic attack on the (η^3 -allyl)palladium complex. We have shown that predictions about the stereoselectivity⁵ and regioselectivity⁶ in these reactions can be aided by molecular mechanics calculations. However, fast dynamic equilibria in the (η^3 -allyl)palladium moiety complicate these predictions.⁷ Further knowledge about the equilibria is therefore desirable and in this paper we would like to report on results with some cyclohexenylpalladium complexes prepared by nucleophilic addition to 1,4-cyclohexadienes (Scheme 1).⁸



Scheme 1.

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We have recently studied the chair–boat equilibrium in complexes of type **1** by molecular mechanics and NMR methods.⁹ It was found that the observed couplings can be rationalized by a rapid equilibrium between chair and boat conformations. Methods of estimating the position of equilibrium were also presented. However, no attempt was made to determine the *rate* of ring inversion. It is known that the rate of nucleophilic attack on (η^3 -allyl)palladium complexes in some cases is comparable to the rate of isomerization in these complexes.^{7b,10} It has also been reported that the conformations of (η^3 -cyclo-

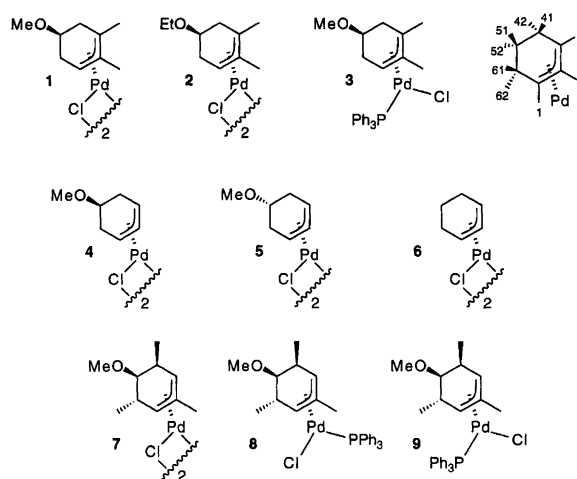


Fig. 1. The compounds studied in this work. The numbering of substituents in the cyclohexenyl moiety is shown top right. In the methylenes, protons *trans* to palladium have a second index of '1' (e.g., H⁵¹), those *cis* to palladium have a second index of '2' (e.g., H⁵²). When a carbon has only one proton bound to it, the second index is left out (e.g., H⁵ in all structures except **6**).

hexenyl)palladium complexes govern the mode of attack by acetate.¹¹ We therefore decided to study the rates of the equilibria in (η^3 -cyclohexenyl)palladium complexes (Fig. 1) by low temperature NMR spectroscopy. To complete the understanding of the reaction in Scheme 1, we have also investigated the apparently anomalous reaction in the parent system, where a *cis* product is formed in addition to the normal *trans* product (Scheme 2).



Results and discussion

Low temperature NMR. The interconversion of the boat and chair conformations of cyclohexane and its derivatives is the classic case of fluxionality in organic chemistry.¹² The equilibrium between an axial and an equatorial conformer for a monosubstituted cyclohexane can be slowed sufficiently to be readily observable in the ^1H NMR spectrum at $\approx -60^\circ\text{C}$.¹³ We felt, therefore, that it might be possible to freeze out the fluxionality of the η^3 -cyclohexenyl ring and so we began by looking at the variable-temperature ^1H NMR spectra of **1** and the 5-ethoxy homolog (**2**).

Upon cooling, the resonances for the ring protons in the ^1H NMR spectra (400 MHz) of both these complexes already show broadening at 0°C . By -80°C in toluene- d_6 , the ring protons become several masses of essentially uninterpretable peaks. The resonances for any single methyl is split into four singlets which appeared to be grouped as one pair of major peaks and one pair of very slightly less abundant minor peaks (ratio $\approx 54:46$ by peak height). Since both complexes exhibit the same behavior with the peak heights being similar, it is highly unlikely that it is ring fluxionality that is being observed. Instead, we believe we are seeing interconversion between various dimeric species. Similar complex behavior has been observed before but the results have not been equally easy to interpret.¹⁴

Taking **1** as the example, the (η^3 -cyclohexenyl) PdCl monomeric unit exists in two enantiomeric forms. Dimerizing all possible combinations of these units, including putting rings either *cis* or *trans* relative to the Pd_2Cl_2 bridge, produces the four possible diastereomers of **1** (as well as their enantiomers) shown in Fig. 2.

These isomers could in principle exhibit a pairwise *syn-syn*, *anti-anti* exchange (an apparent rotation), a process that is known to be fast in many (η^3 -allyl)palladium complexes,^{7a,15} and has been shown to be catalyzed by small amounts of free chloride,^{7a,16} which may very well be present here. However, any other interconversion must involve exchange of enantiomeric partners. This could occur either through complete cleavage of the Pd_2Cl_2 bridge or, less likely, by exchange of η^3 -cyclohexenyl

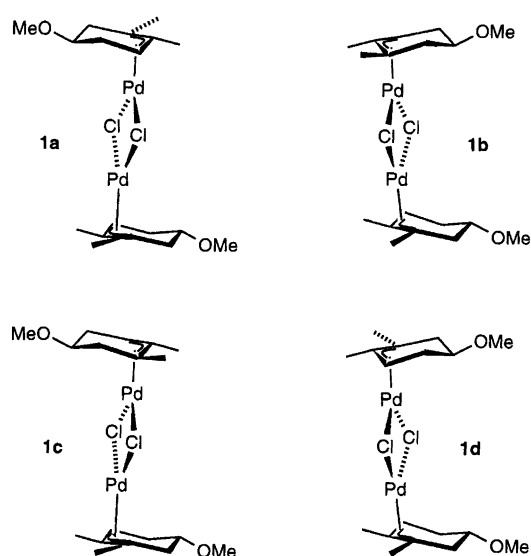


Fig. 2. The four possible diastereomeric forms of **1**, all of which interconvert rapidly.

ligands. Interestingly, the rings in each dimer are magnetically equivalent, since each dimer has a symmetry element which relates the pair of rings and there is no *J* coupling between the rings. Consequently, only one set of resonances would be observed in the ^1H NMR spectrum for each dimer and it is essentially impossible to assign specific peaks to specific dimers. Because of the existence of these four diastereomeric forms of the dimer, it was impossible to observe any ring fluxionality and so monomeric Lewis base derivatives were considered.

Lewis base adducts. Four Lewis bases, pyridine, $\text{P}(\text{OMe})_3$, $\text{P}(\text{OPh})_3$ and PPh_3 , were added in aliquots to solutions of **1** in CDCl_3 and the results observed by ^1H NMR spectroscopy.

As soon as a small amount of pyridine was added (ca. 0.15 equiv.), many of the characteristic resonances for the ring protons broadened significantly, although that for H^5 did not. Upon further addition, the peaks broadened further and then sharpened again until they became well resolved at ≈ 2 equiv., with no further change upon reaching 4 equiv. The final spectrum was superficially very similar to the original, but closer inspection showed that there had been slight, but significant changes. For example, the characteristic triplet of triplets for H^5 had moved from 4.22 to 4.26 ppm, with an accompanying change in the observed coupling constants from 7.8 and 6.0, to 8.0 and 5.8 Hz, respectively. A ^1H spectrum of this final mixture at -60°C showed broad resonances for all cyclohexenyl ring protons, but no broadening of the Me resonances.

Rather different behavior was observed when $\text{P}(\text{OMe})_3$ was used. Addition of a deficiency of $\text{P}(\text{OMe})_3$ resulted in the observation of two sets of sharp resonances in the

^1H NMR spectrum, one of which was due to dimer and the other undoubtedly to the monomeric Lewis base adduct (Me^1 was a doublet with $J \approx 15$ Hz due to ^{31}P coupling). When a slight excess of the phosphite was present, one set of broadened ring resonances was observed.

Taken together, these results suggest that with both Lewis bases, monomeric adducts are formed and that the bases exchange on the NMR timescale. However, because exchange in the pyridine case was observed with less than one equivalent, this must involve cleavage of the N–Pd bond, which could possibly be effected by trace amounts of excess chloride in solution. We know from previous studies on palladium allyls that the exchange of non-allyl ligands is very efficiently catalyzed by small amounts of chloride.¹⁷ In contrast, the exchange was not observed with $\text{P}(\text{OMe})_3$ until after a slight excess had been added, indicating a much stronger bond with phosphites than with pyridines, in accordance with a hard- and soft-ligand point of view. These exchange processes make both pyridine and $\text{P}(\text{OMe})_3$ unsuitable for studying the potential fluxionality of the η^3 -cyclohexenyl ring.

The situations with $\text{P}(\text{OPh})_3$ and PPh_3 are much better. With both these ligands, there is no broadening of peaks and therefore no sign of exchange on the NMR timescale with either deficiencies or excesses (up to fourfold). However, serious overlapping of the resonances of H^{42} and H^{61} in the case of $\text{P}(\text{OPh})_3$ addition made PPh_3 the base of choice for further study.

The compound chloro(5-methoxy-1,2-dimethyl-1-3- η^3 -cyclohexenyl)triphenylphosphinepalladium (**3**) forms instantly upon addition of one equivalent of PPh_3 per Pd to the dimer **1**. The product may be isolated as pale-yellow crystals from CH_2Cl_2 – Et_2O solution. It does not appear to be air-sensitive, but is somewhat more thermally sensitive than the parent dimer and is best stored under an inert atmosphere, cold (-25°C). Both the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra show that only one product is formed and inspection of molecular models shows that it is likely to have structure **3** where the phosphine coordinates *trans* to Me^1 of the η^3 -cyclohexenyl ligand. This is confirmed by the relative ^1H chemical shifts for **1** and **3**, since the resonances for the protons on positions 2, 3, 4 and 5 all show substantial movement upfield upon PPh_3 coordination due to a marked ring current effect¹⁸ from the phosphine phenyl groups. This effect is particularly noticeable on H^3 and H^{42} , just as expected from a model.¹⁹ The couplings of the protons and carbons to phosphorus are also informative, with nuclei *trans* to ^{31}P showing much larger coupling than those *cis*, as expected,²⁰ and *exo* proton couplings with larger J values than *endo* protons (e.g., $J_{\text{H}^{62},\text{P}} = 6.3$ Hz). Note also the large range of four-bond ^1H , ^{31}P couplings in this compound, with the values ranging from 1.7 to 15.0 Hz. The ^1H couplings in the saturated part of the cyclohexenyl ring are shown in Table 1.

As was pointed out in our previous paper,⁹ $J_{42,5}$ (and $J_{62,5}$) is almost independent of conformation, whereas $J_{41,5}$ (and $J_{61,5}$) is a good indicator of the relative amounts

Table 1. Selected observed coupling constants in **3**, **8**, and **9**

Coupling	Adduct	Observed (Hz)	Parent dimer	Observed ^a (Hz)
$J_{41,5} = J_{5,61}$	3	8.9	1	7.6
$J_{42,5} = J_{5,62}$		6.0		5.8
$J_{42,5}$	8	5.7	7	6.0
$J_{5,61}$		10.0		6.0
$J_{42,5}$	9	6.2	7	6.0
$J_{5,61}$		10.3		6.0

^a Ref. 10.

of boat and chair conformers in equilibrium. It is probable that on going from a dimeric to a monomeric Lewis base adduct, the structures of the major conformations (chair and boat) are relatively unaffected, but their relative energies are shifted. This is in accordance with the data in Table 1, where it can be seen that $J_{42,5}$ is almost unchanged by addition of the Lewis base (5.8 Hz in **1**, 6.0 Hz in **3**), whereas $J_{41,5}$ increases from 7.6 to 8.9 Hz. For the dimer (**1**), this coupling was calculated to be ≈ 3 Hz in the boat and ≈ 10 Hz in the chair conformation.⁹ It is dangerous to draw detailed conclusions about the exact energy difference between the chair and boat conformations, but it is clear that the chair is energetically favored for complex **3**. From the range of observed couplings for similar dimeric complexes (up to 10.7 Hz),^{1,8,9} it seems reasonable to assume that a substantial amount of boat is still present in equilibrium. It was therefore hoped that both conformations should be visible in the low-temperature studies.

Cooling a solution of 12 mg of **3** in 1 ml of CHFCl_2 –4% acetone- d_6 in a flame-sealed NMR tube down to -100°C showed no significant change in either the ^1H or $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum beyond the usual dependence of chemical shift on temperature. This supports our conclusion that the fluxionality observed for the dimer is due to monomer exchanges and not to ring conformational effects. Below -100°C , the ^1H spectral peaks were too broad to be useful, while the resonances in the $^{13}\text{C}\{^1\text{H}\}$ spectrum started to split. At -100°C , the CHFCl_2 doublet started to show some splitting, as did C^3 . By -130°C , the CHFCl_2 peaks separated into two equal intensity pairs of peaks and all peaks due to the η^3 -cyclohexenyl carbons of **3** except Me^2 split by varying amounts into peak pairs of equal intensity (it was also apparent from the peak intensities that most of the compound had precipitated out of solution). Even by -130°C , the acetone- d_6 methyl septet showed none of this splitting. We cannot attribute any of this splitting to conformational changes in the ring; freezing out a conformational change should result in peak pairs of unequal intensity, probably with the chair as major component (*vide supra*), and the solvent should not split at all. In addition, the two conformations would have different

coupling patterns, which is not the case. We therefore believe the observed splitting is due to solvent–solvent and solvent–solute hydrogen bonding effects.²¹ Decoalescence should still be visible had it occurred. Obviously, if our assumptions are correct, the ring inversion is too fast to be frozen out even at -130°C . Dihedral driver calculations²² for complex **1** indicate an energy of activation of $\approx 6 \text{ kcal mol}^{-1}$ for the ring inversion. With such a low activation energy, the chemical shifts would have to be separated by more than 500 Hz to give decoalescence at -130°C . The failure to observe this flip is therefore readily understood.

1,3,5-Trimethyl-1,4-cyclohexadiene derivatives. In an effort to circumvent the problem of the high rate of fluxionality, we tried the system using the sterically more crowded 1,3,5-trimethyl-1,4-cyclohexadiene. It has been shown that increasing the steric crowding on a cyclohexene derivative substantially raises the coalescence temperature. For example, *cis*-4,5-dimethoxycarbonylcyclohexene begins to show broadening at -115°C (^1H NMR, 60 MHz) and decoalesces at -135°C ,¹³ as compared with polydeuterated cyclohexenes which show decoalescence around -160°C (^1H NMR, 60 MHz).^{13,23} Calculations²² also verify that the inversion barrier is slightly higher for **7** than for **1**.

When **7** was reacted with PPh_3 , two isomers **8** and **9** were produced (Table 1). These compounds have essentially the same properties as **3**. The two isomers do not interconvert, as recrystallization enriches the product in the major isomer by going from an initially formed 3:1 to a final 4:1 mixture.²⁴ The major isomer (**8**) is the one where the phosphine has ended up *cis* to the *exo* methyl group on C^4 , with the minor just the opposite – exactly what one would expect on the basis of molecular models. This assignment is confirmed by the observation of the expected ring current effects (*vide supra*) on the chemical shifts of the ring substituents. The various couplings to phosphorus show effects similar to those observed for **3**, with four-bond ^1H , ^{31}P couplings spanning an even larger range here (0 to $\approx 20 \text{ Hz}$).

The shift in the ‘indicator’ coupling is even more pronounced here than for the previous system. The coupling $J_{5,61}$ increases from 6 Hz to $\approx 10 \text{ Hz}$ when the ligand is added. This large, almost purely axial–axial coupling indicates that the monomeric complexes **8** and **9** exist predominantly in chair conformations. Unfortunately, the increased steric bulk does not raise the coalescence temperature for ring fluxionality enough to be observable with our equipment, as exactly the same behavior was observed in the low-temperature ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **8** and **9** as for **3**. This again suggests a very low activation energy, or perhaps a very low relative abundance of the boat conformation for these complexes.

Abnormal product formation. We finally turned to the apparent formation of the *cis* product (**5**), formed in the reaction of palladium-assisted nucleophilic addition to

1,4-cyclohexadiene (Scheme 2).⁹ If product **5** is formed directly, the mechanism should involve direct migration of a methoxy group from palladium to a coordinated olefin.

Although this type of mechanism was initially suggested for the Wacker process and related reactions, there are not many clear cut examples. Instead, external attack of the nucleophile is generally observed.²⁵ Alternatively, the *cis* product **5** could be formed from the *trans* product **4** by reversible displacement of coordinated palladium by external palladium(0).^{8,14b} The presence of palladium(0) in the reaction mixture could come about by formation of palladium hydrides, followed by reductive elimination of hydrogen or hydrogen chloride. That palladium(0) is formed is evident from the formation of a palladium mirror in the reaction flask after a couple of days. The formation of free palladium hydride species is in fact indicated by the presence of the η^3 -cyclohexenyl complex **6**, presumably formed by addition of palladium hydride to 1,4-cyclohexadiene. In order to clarify the mechanism for the formation of **5**, the reaction between 1,4-cyclohexadiene and methanol- d_4 and palladium chloride was monitored by NMR spectroscopy using the methanol peak as an internal standard.

In this experiment it was also shown that dehydrogenation of 1,4-cyclohexadiene to benzene took place (ca. 45% yield), indicating this to be the source of palladium hydride.

In the initial phase, only compounds **4** and **6** could be detected. The concentration of **6** continued to increase throughout the reaction, whereas the formation of **4** was fast initially and then slowed down. After about a day at -15°C , the concentration of **4** started to decrease. At this point, compound **5** started to form. This suggests, as believed earlier,^{8,14b} that **5** is formed from **4** and gives support to the idea of displacement of coordinated palladium by external palladium(0).

Conclusions

The difficulty in freezing out the fluxionality of the η^3 -cyclohexenyl ring indicates a very rapid conformational change between chair and boat conformations. This is supported by geometry and energy calculations,^{9,22} together with the observed coupling constants that have values in between those of the pure boat and chair conformations. Very low coalescence temperatures have also been observed for related systems.²⁷ Our inability to observe any relevant decoalescence at -130°C for **3** is therefore readily understood and the energy barrier to ring flipping may be as low as or even lower than that of cyclohexene. Unfortunately, the solubility of **3** and our instrumentation prevented us from going to lower temperatures. The observed splitting upon cooling seems to arise instead from isomeric dimers.

The previous suggestion⁸ that **5** is formed via attack of $\text{Pd}(0)$ on **4** is supported by experiment.

Experimental

General. The general experimental procedures used and the preparations of the palladium dimers have been described previously.⁸ NMR spectra were run on a Bruker AM 400 spectrometer equipped with a B-VT1000 variable temperature unit. ¹H and ¹³C{¹H} (composite-pulse broad-band ¹H decoupled ¹³C) NMR spectra were assigned with the aid of heteronuclear correlation and double-quantum filtered phase sensitive COSY experiments. All chemical shifts are quoted in ppm downfield (δ) from Me₄Si and all coupling constants (*J*) in Hz.

PPh₃ derivatives of 1 and 7 (3, 8 and 9). To a stirred yellow solution of dimer **1**, (27.7 mg, 49.2 μmol) in 2.5 ml CH₂Cl₂ was added one equivalent of PPh₃ (25.9 mg, 98.5 μmol), whereupon the color of the solution immediately lightened. The solution was then evaporated to dryness under vacuum and the resulting oil recrystallized at -25°C from a 1:2 mixture of CH₂Cl₂-Et₂O to give a yellow microcrystalline product of **3**. Compounds **8** and **9** were prepared in the same way, except prior to crystallization, the glassy product was flash-chromatographed through a 2 × 15 cm silica column using a gradient solvent elution system starting with a 90:10 petroleum ether-ethyl acetate mixture and finishing with a 50:50 mixture. Compounds **8** and **9** were then crystallized from Et₂O at -25°C to give yellow microcrystals.

3: ¹H NMR (400 MHz, CDCl₃): δ 7.3–7.7 (15 H, 2 m, PPh₃), 4.05 (1 H, tt, *J*_{5,42} = *J*_{5,62} = 6.0, *J*_{5,41} = *J*_{5,61} = 8.9, H⁵), 3.55 (1 H, br dd, *J*_{3,42} = 3.4, *J*_{3,41} = 2.8, *J*_{H¹,P} = 2.4, H³), 3.13 (3 H, s, OMe), 2.72 (1 H, dt, *J*_{6,1,62} = 16.0, *J*_{H⁶²,P} = 6.3, H⁶²), 1.88 (3 H, s, Me²), 1.82 (3 H, d, *J*_{Me¹,P} = 9.1, Me¹), 1.64 (1 H, ddd partially concealed by H⁴², *J*_{H⁶¹,P} = 15.0, H⁶¹), 1.60 (1 H, dddd partially concealed by H⁶¹, *J*_{41,42} = 15.3, *J*_{H⁴²,P} = 1.7, H⁴²), 1.12 (1 H, dddd, *J*_{H⁴¹,P} = 7.1, H⁴¹). ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 133.88 (d, *J*_{C,P} = 13, *ortho* C PPh₃), 133.19 (d, *J*_{C,P} = 39, *ipso* C PPh₃), 130.26 (s, *para* C PPh₃), 128.58 (d, *J*_{C,P} = 10, *meta* C PPh₃), 117.73 (s, C²), 105.46 (d, *J*_{C,P} = 29, C¹), 73.59 (s, C⁵), 72.89 (s, C³), 56.02 (s, OMe), 41.11 (d, *J*_{C,P} = 5, C⁶), 33.37 (s, C⁴), 20.97 (d, *J*_{C,P} = 5, Me¹), 19.99 (s, Me²).

8: ¹H NMR (400 MHz, CDCl₃): δ 7.3–7.75 (15 H, 2 m, PPh₃), 5.14 (1 H, dt, *J*_{1,3} = 2.3, *J*_{1,6} = 2.1, *J*_{H¹,P} = 7.6, H¹), 3.70 (1 H, ddd partially concealed by H⁵, *J*_{3,4} = 4.5, *J*_{3,P} = 2.8, H³), 3.67 (1 H, dd partially concealed by H³, *J*_{4,5} = 5.7, *J*_{5,6} = 10.0, H⁵), 3.05 (3 H, s, OMe), 1.88 (3 H, s, Me²), 1.70 (1 H, ddqd, *J*_{H⁶,Me⁶} = 6.7, *J*_{H⁶,P} ≈ 20, H⁶), 1.67 (1 H, qdd, *J*_{H⁴,Me⁴} = 6.9, H⁴), 1.42 (3 H, d, Me⁶), 0.68 (3 H, d, Me⁴). ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ PPh₃ resonances not assigned 120.34 (d, *J*_{C,P} = 5, C²), 99.40 (d, *J*_{C,P} = 32, C¹), 83.18 (s, C⁵), 81.60 (s, C³), 56.34 (s, OMe), 36.79 (d, *J*_{C,P} = 5, C⁶), 34.56 (s, C⁴), 23.21 (s, Me²), 17.77 (s, Me⁶), 16.15 (d, *J*_{C,P} = 3, Me⁴).

9: ¹H NMR (400 MHz, CDCl₃): δ 7.3–7.75 (15 H, 2 m, PPh₃), 5.20 (1 H, ddd, *J*_{1,3} = 2.6, *J*_{3,4} = 4.8, *J*_{H³,P} = 7.5, H³), 3.82 (1 H, td partially concealed by H⁵,

*J*_{1,6} = 1.5, *J*_{H¹,P} = 2.5, H¹), 3.79 (1 H, dd partially concealed by H¹, *J*_{4,5} = 6.2, *J*_{5,6} = 10.3, H⁵), 3.26 (3 H, s, OMe), ≈ 2.90 (1 H, qddd, *J*_{H⁴,Me⁴} = 6.9, *J*_{H⁴,P} = 3.4, H⁴), 1.86 (3 H, s, Me²), ≈ 1.36 (1 H, dqdd, *J*_{H⁶,Me⁶} = 6.7, *J*_{H⁶,P} ≤ 4.5, H⁶), 0.90 (3 H, d, Me⁴), 0.53 (3 H, d, Me⁶). ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ PPh₃ resonances not assigned 120.20 (d, *J*_{C,P} = 6, C²), 94.78 (d, *J*_{C,P} = 35, C³), 87.40 (s, C¹), 83.13 (s, C⁵), 56.70 (s, OMe), 36.13 (s, C⁶), 35.54 (d, *J*_{C,P} = 5, C⁴), 23.35 (s, Me²), 17.87 (s, Me⁶), 16.50 (d, *J*_{C,P} = 12, Me⁴).

Very low temperature (< -80°C) NMR studies. Samples were made up by placing a small amount (10–12 mg) of the solid material in a 5 mm, sealable NMR tube, adding 2 drops of acetone-*d*₆ and then cooling the tube to -78°C under argon. A vacuum was then briefly applied and then the required volume of CHFCl₂ solvent (b.p. = 8°C, m.p. ≈ -135°C) was condensed in the tube. The mixture was then frozen in a liquid N₂ bath and the NMR tube flame-sealed under vacuum. The tube was then allowed to warm to room temperature in a safe place in case of possible explosion (ideal gas pressure of CHFCl₂ at 25°C = 810 mmHg).

Monitoring of the formation of 4, 5, and 6 by NMR. To a cold (-78°C, dry ice-acetone), stirred yellow slurry of 130 mg (0.5 mmol) of bis(acetonitrile)palladium dichloride, 46 mg (0.46 mmol) of KHCO₃, and 15 mg (0.09 mmol) of cupric chloride in 3 ml of MeOH-*d*₄ was slowly added (dropwise, 3 min) a solution of 33 mg (0.41 mmol) of 1,4-cyclohexadiene in 2 ml of MeOH-*d*₄ and then the reaction vessel containing the yellow slurry was sealed and placed in a freezer at -19°C. NMR samples were taken out after 9, 20, 90, 140 and 200 h.

Acknowledgements. Support from the Trygger Foundation and the Danish Medical Research Council is gratefully acknowledged. J. D. O. thanks the Royal Institute of Technology for a research scholarship.

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Received February 13, 1995.