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cis-Addition of a palladium-carbon bond to coordinated olefins

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Insertion of olefinic functions into metal–carbon bonds has often been represented as a key propagation step in the transition-metal catalysed polymerisation and oligomerisation of unsaturated hydrocarbons. However, mechanistic details have in the most part been deduced from the nature of the purely organic polymers (or oligomers) formed, and a *cis*-addition of the metal–carbon bond to a coordinated olefin has frequently been postulated. We have now established the nature of the first stable 1/1 adducts arising from addition of a palladium–allyl bond to coordinated olefins. The structure of these adducts provides the first direct evidence of a stereospecific *cis*-addition of a metal–carbon bond to a coordinated olefin.

We have previously established that addition of 1,2- or 1,3-dienes to solutions of (π-allyl)Pd (X) (I) causes the NMR signals due to the allylic *syn*- and *anti*-protons to collapse due to a rapid $\pi \rightarrow \sigma \rightarrow \pi$ process involving a σ-allylic intermediate, similar to (II)[1]. We now report that addition of a one molar equivalent of norbornadiene to solutions of (I), [X = hexafluoroacetylacetonate], in $CHCl_3$ or C_6H_6, at 37° likewise causes collapse of the *syn*- and *anti*- proton resonances, indicating rapid, reversible formation of (II). Further reaction of (II) rapidly occurs to give the novel enyl palladium complexes (III). Norbornene likewise inserts into the allyl–palladium bond to give enyl complexes structurally analogous to (III). Under similar conditions styrene, cyclohexene, 1,4-cyclohexadiene, or 1,5-cyclooctadiene readily promote formation of σ-allylic species, similar to (II), but no further reaction to give enyl complexes is observed.

Microanalyses, mass spectra, and ^{1}H NMR data of (III) are consistent with the structure shown. NMR data of substituted norbornenes and norbornanes have been well documented[2], and the pertinent NMR data for (IIIa) and (IIIb) are summarized in Table 1.

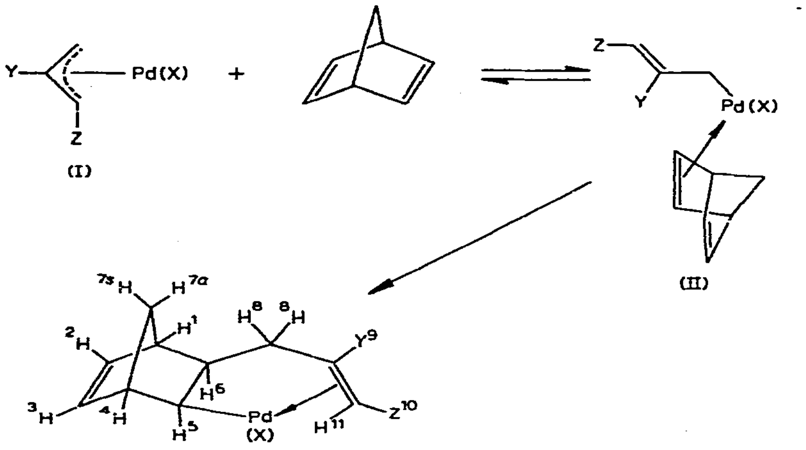
TABLE I

100 MHz ^{1}H NMR DATA FOR COMPLEXES (III) IN C_6D_6 [J VALUES IN Hz]

Complex	$\tau(H_2 + H_3)$	$\tau(H_5)$	$\tau(H_6)$	$\tau(H_{10})$	$\tau(H_{11})$	$J_{5,6}$	$J_{1,6}$	$J_{4,5}$	$J_{9,10}$	$J_{9,11}$
IIIa	4.18	7.52	9.06	6.10	6.52	7	<2	<2	9	16
IIIb	4.22	7.62	9.11	6.42	6.72	7	<2	<2	–	–

The magnitude of $J_{5,6}$ indicates a mutually *cis*-configuration for these protons. Small values of $J_{1,6}$ and $J_{4,5}$ indicate that H_5 and H_6 occupy *endo*-positions. [Coupling of H_1 and H_4 with *exo*-protons is usually 3–4 Hz.] In agreement, weak coupling is also observed between H_5, H_6 and H_{7s}. The resonances assigned to H_{10} and H_{11} are shifted to higher field than expected for a free olefin, indicating coordination of *this* olefin to the metal. In contrast the chemical shifts of H_2 and H_3 are similar to those observed in free norbornene. An *exo–endo*-configuration for (III) makes coordination of the exocyclic olefin sterically impossible, and is also incompatible with the observed coupling constants. Reactions with terminally substituted π-allyl complexes (I) indicate that the least substituted terminal carbon atom of the allyl moiety becomes attached to the bicyclic ring system (IIIc). Thus the reaction involves direct carbon transfer from palladium to the coordinated olefin, as observed in the case of 1,2-diene insertion[1].

The mass spectra of complexes (III) show parent ion peaks, the base peaks corresponding to loss of hexafluoroacetylacetone. In addition peaks corresponding to the loss of cyclopentadiene, via a retro-Diels–Alder reaction, are observed. The products derived from norbornene insertion do not exhibit this latter breakdown.



(I)

(II)

(IIIa, Y=Z=H;
IIIb, Y=CH$_3$, Z=H;
IIIc, Y=H, Z=CH$_3$)

X= hexafluoroacetylacetonate

The most sterically favoured mode of coordination of norbornene to transition metals is via the *exo*-face of the double bond[3,4]. Mercuric carboxylates are known to add to norbornene, giving *cis-exo*-substituted products[4,5].

The reactivity of bicyclic olefins may be attributed to relief of ring strain. A concerted transfer mechanism is favoured since stabilization of an incipient carbonium ion in a two-step transfer process would be favourable in styrene, which does not react.

Preliminary investigations indicate that allylic platinum complexes undergo analogous reactions and further studies of insertion of strained olefins into metal–ligand bonds are in progress.

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