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Changing selectivity in palladium-catalyzed reactions involving oxidation state IV. A new synthesis from iodobenzene and norbornene

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Abstract

The formation of organopalladium intermediates in a catalytic reaction between iodobenzene and norbornene, involving a palladium(0)–(II)–(IV)–(II)–(0) sequence, can be directed towards preferential formation of product V or IV.

The chemistry of palladium(IV) complexes [1,2] has recently attracted much interest from both synthetic and mechanistic points of view. Palladium(IV) complexes were postulated [3–11] as intermediates in several reactions. Catalysis involving palladium(IV) species was recently demonstrated [12] in the case of a palladium(IV) metallacycle.

We previously reported [11] that aryl bromides react with strained olefins such as norbornene in the presence of $Pd(PPh_3)_4$-KO^tBu to give compound III via an alkylaromatic palladacycle. According to our proposal the latter undergoes further oxidative addition of the same aryl halides, thus forming a palladium(IV) complex. In turn the latter reverts to two palladium(II) species, which both undergo ring-forming aromatic substitution, to give compound III in the case of halobenzene and to isomeric substituted derivatives of III in the case of other aryl halides (equation 1, non participative ligands are omitted for simplicity).

Model complexes of the palladium(IV) intermediates in this reaction have been isolated [12,13], and it has been shown that the phenanthroline ligand can orient the attack of an organic halide on the first formed palladium(II) metallacycle so that only one isomer of the palladium(IV) metallacycle is formed [13], and the latter can then undergo conversion into a single palladium(II) isomer (corresponding to II).

In a recent paper [14] it was reported that under different conditions ($Pd(OAc)_2$, K_2CO_3, Bu_4NBr, dimethylformamide (DMF), 60–100 °C), intermediate II can be made to undergo a new oxidative addition before final ring closure to IV (equation 2). Apparently intermediate II, containing a palladium–norbornyl bond, is formed in preference to I, which contains an aryl–palladium bond.

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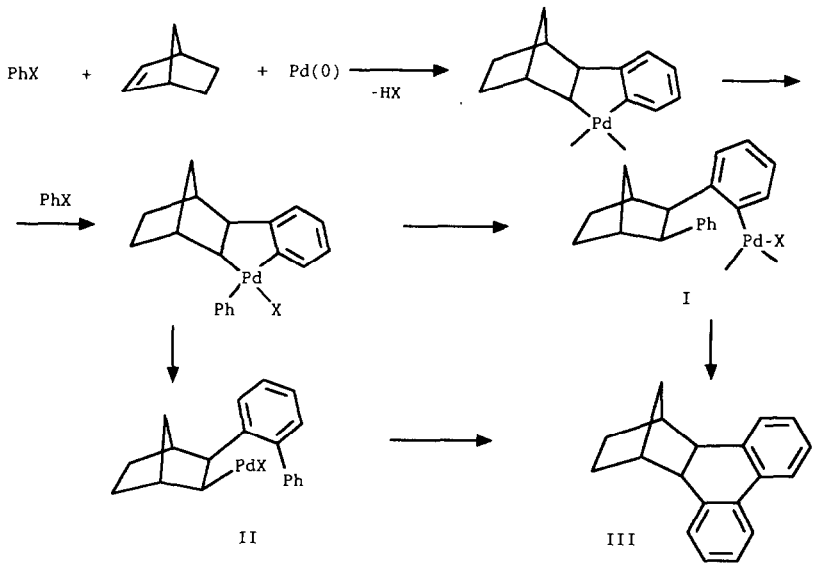
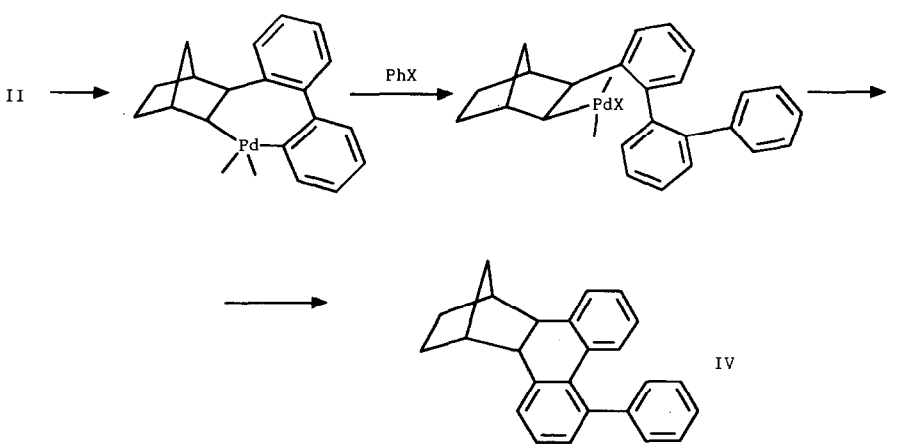


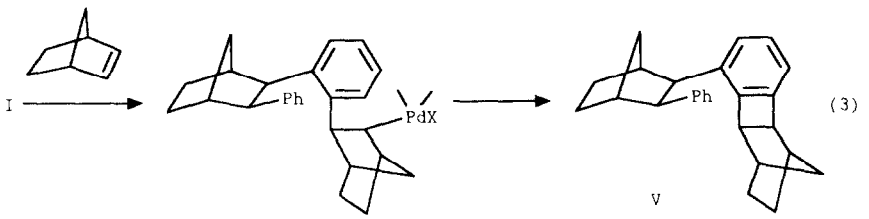
(1)

To ascertain why intermediate II rather than I was involved we compared the results obtained with palladium(0) complexes with and without triphenylphosphine as ligand. While palladium(0) dibenzylideneacetone and potassium carbonate in DMF reacted to a small extent (less than 10%), to give very predominantly compound IV, along with a small amount of a new compound (V), the use of palladium(0) with triphenylphosphine as ligand led to V in substantial yield. Thus stirring a mixture of $Pd(PPh_3)_4$, 1 mmol, norbornene, 24 mmol, iodobenzene, 20 mmol, and potassium carbonate, 60 mmol at 80 °C in DMF (Pd = 0.01 *M*), gave V in 52% isolated yield, together with a condensed benzocyclobutene (1,2,3,4,4*a*,8*b*-hexahydro-1,4-methanobiphenylene [15]), phenylnorbornane (2 : 1) (ca 10%) and IV (7%). Minor amounts of a 5-phenyl derivative of the above-mentioned methano-



(2)

biphenylene [16], III, and a diastereoisomer of V are also present. The structure of V (all *exo*) shows clearly that it is derived from the aryl-palladium intermediate I (equation 3).



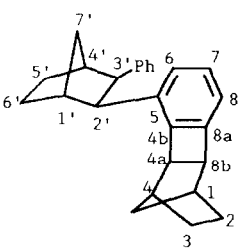
The major diastereoisomer has been characterized by ^{1}H and ^{13}C NMR spectroscopy.

The dominant factor responsible for the change in selectivity towards the process leading to IV turns out to be the presence of the triphenylphosphine ligand, which apparently favors the formation of the relevant arylpalladium(IV) intermediate leading to I. Triphenylphosphine influences either the stereochemistry of the oxidative addition to the palladium(II) metallacycle or the subsequent isomerization to a preferential stereoisomer. The triphenylphosphine-stabilized intermediate I has little tendency to undergo aromatic substitution, and prefers the insertion of a new molecule of norbornene before final ring closure of the norbornylpalladium bond on the aryl group.

Under the conditions used the reaction also differs from that of equation 1, which requires potassium tert-butoxide as base and a higher temperature. These factors cause cyclization of intermediates I and II to occur at an earlier stage, with formation of compound III.

In conclusion the results reported here show that the selectivity of a catalytic reaction involving a palladium(IV) complex can be controlled by using an appropriate ligand to drive the reaction preferentially towards a particular palladium(II) species resulting from reductive elimination. In the present case the result is a triphenylphosphine-induced diversion from aromatic substitution to double bond insertion at the stage of intermediate I.

Analytical data for 1,2,3,4,4a-exo-*8b*-exo-*hexahydro-5-(2'*-exo-*(3'*-exo-*phenyl)norbornyl)-1,4-methanobiphenylene*



Norbornene bridges can be mutually *syn* or *anti*. Which is which of these diastereoisomers has not been established, so the drawing may not represent the major product. ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ 7.00–6.85 (5H, m, phenyl ring protons); 6.78 (1H, H7, dd, $J = 7.8, 7.1$ Hz); 6.63 (1H, H6 or H8, d, $J = 7.8$

Hz); 6.55 (1H, H8 or H6, d, $J = 7.1$ Hz); 3.30 (1H, H2′ or H3′, m); 3.15 (1H, H3′ or H2′, m); 3.00 (1H, H4a or H8b, br d, $J = 4.0$ Hz); 2.90 (1H, H8b or H4a, br d, $J = 4.0$ Hz); 2.59 (1H, H1′ or H4′, br s); 2.44 (1H, H4′ or H1′, br s); 2.29 (1H, H7′-*syn*, partly overlapped); 2.26 (1H, H1 or H4, br s); 2.12 (1H, H4 or H1, br s); 1.80–1.66 (2H, H5′-*exo*, H6′-*exo*, m); 1.62–1.40 (7H, H5′-*endo*, H6′-*endo*, H2-*exo*, H3-*exo*, H7′-*anti*, m); 1.18–1.07 (2H, H2-*endo*, H3-*endo*, m); 0.82 (1H, H methano *anti*, d further split, $J = 10.1$, 1.5 Hz); 0.57 (1H, H7 methano *syn*, d further split, $J = 10$, 1.6 Hz). ^{13}C NMR (25.2 MHz, $CDCl_3$, TMS), ^{13}C–^{1}H correlation and DEPT. Positive (CH) and negative (CH_2) phases are indicated by + and −, respectively; * indicates that the signal (quaternary carbon) disappears: δ 145.6(*); 144.6(*); 142.9(*); 138.3(*); 128.9(+); 128.7(+); 127.3(+); 127.0(+); 126.9(+); 125.1(+); 118.7(+); 55.0 (+, C2′ or C3′); 51.2 (+, C3′ or C2′); 50.5 (+, C4a or C8b); 49.0 (+, C8b or C4a); 43.0 (+, Cl′ or C4′); 41.6 (+, C4′ or Cl′); 37.2 (−, C7′); 37.1 (+, Cl or C4); 36.5 (+, C4 or Cl); 31.8 (−, C methano); 31.2 (−, C5′ or C6′); 30.4 (−, C6′ or C5′); 28.1 (−, C2 or C3); 28.0 (−, C3 or C2). MS (70 eV): M^+ 340(25), 300(19), 299(100), 233(20), 167(25), 165(27), 153(19), 152(18), 143(20), 141(32), 129(25), 128(18), 117(20), 115(30), 91(60), 67(28).

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