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Preliminary communication

COMPETITIVE PROCESSES IN PALLADIUM-CATALYZED C—C BOND FORMATION

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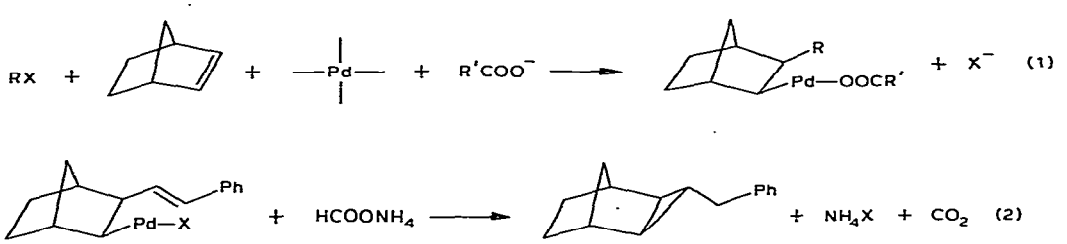
Summary

A palladium—carbon bond, stable towards hydrogen elimination, undergoes various insertion and reductive elimination reactions, depending on availability of facile reductive elimination steps.

Our current interest in multistep insertion processes has led us to examine the ability of a Pd—C bond which is stable towards hydrogen elimination to undergo alternative reaction paths. Formation of a suitable bond can be easily achieved by carboxylato anion-promoted insertion of norbornene into vinyl- or aryl-palladium bonds Pd—R (eq. 1). The Pd—C bond thus formed cannot readily undergo elimination, and so reacts by other routes, depending on the nature of the R group. We previously reported [1] that when R is a styryl group (from 1-bromostyrene) the reaction can lead to formation of a cyclopropane ring, provided that a hydride source is present to terminate the process (eq. 2).



We now observe that, if R is an aliphatic 1-olefin, cyclopropane formation can also take place in the absence of a hydrogen transfer agent, an alternative path, consisting of hydrogen elimination from the allylic carbon, being fol-

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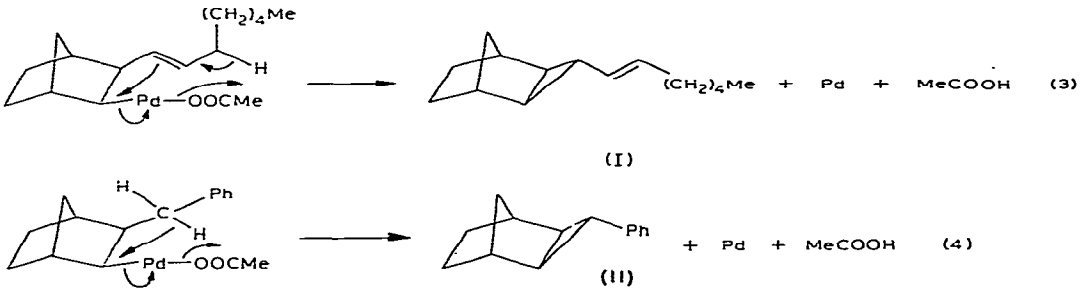
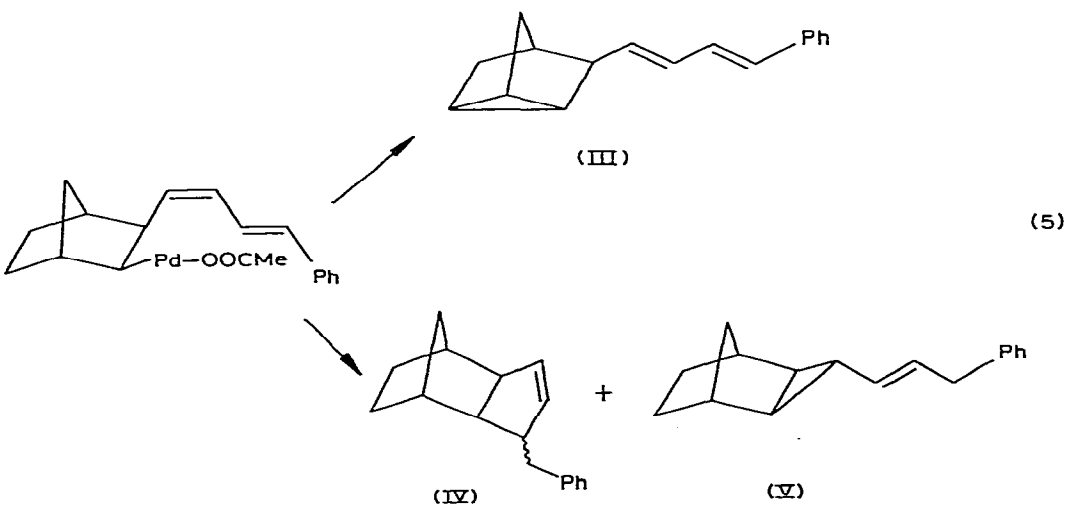
lowed. Thus 1-bromo-1-octene in anisole at 80°C for 8 h gives a condensed cyclopropane (I) with 56% selectivity (eq. 3). Bromide conversion is 54%.

Even more interestingly, cyclopropane ring formation can occur under the same conditions by a quite different mechanism when R is a benzyl group (from benzyl halides). In this case hydrogen elimination must occur by displacement of the metal to give II with 52% selectivity (eq. 4). Conversion is low, however, and most of the benzyl bromide used is found as the acetate.

To our knowledge this and the following one are the first cases of catalytic activation of a saturated C—H bond in a termination step.



When R is the 1-*Z*-3-*E*-4-phenylbutadienyl group, the main product (III) also results from cyclopropane ring closure (32% selectivity at 60°C for 5 h) but this time a saturated C—H bond of the norbornane skeleton is involved (eq. 5). A compound of M^+ 282 (24% selectivity) corresponding to termination by acetate addition to the norbornene insertion complex, is the major component among several unidentified by-products. The bromide is completely converted under these conditions, and a further increase in the temperature results in a lower selectivity. The expected ring closure to a condensed cyclopentene does not occur to a significant extent, probably because the butadienyl chain reacts so slowly that it has the time to isomerize to the *E,E*-configuration. In agreement with this interpretation, if a hydride source ($HCOONH_4$) is available to provide a faster reductive elimination step, cyclopentene ring formation to IV does occur (49% selectivity at 80°C). Furthermore a condensed cyclopropane (V) is also formed with 24% selectivity.



It thus appears that Pd—C bonds which do not readily undergo hydrogen elimination from β-position are available for alternative pathways, the choice of which is determined by their ability to provide a favorable elimination step. The design of such an elimination step can be relevant for the achievement of catalytic processes.

Additional elimination patterns, involving more complex interactions, such as those occurring with aromatic halides have been observed and will be reported in the near future.

General procedure

Norbornene (3 mmol), the organic halide (3 mmol) and K acetate (3 mmol) are caused to react at 60—80°C in anisole (3 ml) in the presence of $Pd(PPh_3)_4$ (0.1 mmol) for 6—8 h under nitrogen. The products are separated by chromatography on a SiO_2 column, using n-hexane as eluent.

3-(Hept-1-en-1-yl)tricyclo[3.2.1.$0^{2,4}$]octane (I). Mass spectrum (60 eV): M^+ 204, *m/e* 150, 91, 80, 67; ^{1}H NMR (100 MHz, $CDCl_3$, TMS): δ 5.48(dt, *J* 15 Hz, *J* 7 Hz, 1H), 4.90 (dd, *J* 15 Hz, *J* 8 Hz, 1H), 2.32 (m, 2H), 2.18—1.74 (m, 2H), 1.60—1.10 (m, 12H), 1.10—0.50 (m, 6H) ppm; ^{13}C NMR (25.2 MHz, $CDCl_3$, TMS): δ 131.3, 127.9 (vinyl carbons), 35.9 (d, C(1), C(5)), 32.6 (t, CH_2—C=), 31.4(t), 29.5 (t,C(6), C(7), chain CH_2), 28.4 (t, C(8)), 24.2 (d, C(2), C(4)), 22.6 (t), 16.7 (d, C(3)), 14.0 (q, CH_3) ppm.

3-Phenyltricyclo[3.2.1.$0^{2,4}$]octane [2] (II). ^{13}C NMR (25.2 MHz, $CDCl_3$, TMS): δ 142.9, 127.8, 125.6, 124.9 (aromatic carbons), 36.3 (d, C(1), C(5)), 29.3 (t, C(6), C(7)), 28.6 (t, C(8)), 27.6 (d, C(2), C(4)), 18.3 (d, C(3)) ppm.

3-(4-Phenyl-1-*E*-3-*E*-butadien-1-yl)tricyclo[2.2.1.$0^{2,6}$]heptane (III). Mass spectrum (60 eV): M^+ 222, *m/e* 156, 129, 115, 91, 77, 65; ^{1}H NMR (270 MHz, $CDCl_3$, TMS): δ 7.50—7.10 (m, 5H, aromatic protons), 6.75 (dd, *J* 16 Hz, *J* 10 Hz, 1H, HC(3 dienic)), 6.45 (d, *J* 16 Hz, 1H, HC(4 dienic)), 6.27 (dd, *J* 16 Hz, *J* 10 Hz, 1H, HC(2 dienic)), 5.76 (dd, *J* 16 Hz, *J* 7 Hz, 1H, HC(1-dienic)), 2.24 (br d, *J* 7 Hz, 1H, HC(3)), 1.78 (m, 1H, HC(4)), 1.46 (d, *J* 10 Hz, 1H, HC(7)), 1.40—1.25(AB system, 2H, H,HC(5)), 1.20—1.03 (m, 4H, HC(1), HC(2), HC(6), HC(7)) ppm. ^{13}C NMR [3] (25.2 MHz, $CDCl_3$, TMS): δ 137.4, 136.0, 130.3, 129.9, 129.2, 128.3, 126.8, 125.9 (aromatic and dienic carbons), 47.4 (d, C(3)), 34.7 (d, C(4)), 34.1 (t, C(5)), 29.3 (t, C(7)), 14.6 (d, C(2)), 11.4 (d, C(1)), 9.6 (d, C(6)) ppm.

5-Benzyltricyclo[5.2.1.$0^{2,6}$]dec-3-ene (IV). Mass spectrum (60 eV): M^+ 224, *m/e* 133, 91, 67; ^{1}H NMR (100 MHz, $CDCl_3$, TMS) δ 7.45—7.00 (m, 5H), 5.43 (AB system, 2H), 3.40—3.00 (m, 1H), 2.82 (dd, *J* 13 Hz, *J* 6 Hz, 1H), 2.71 (brd, *J* 8 Hz, 1H), 2.53 (dd, *J* 13 Hz, *J* 10 Hz, 1H), 2.35—2.04 (m, 2H), 2.04—1.88 (m, 1H), 1.64—0.90 (m, 6H); ^{13}C NMR (25.2 MHz, $CDCl_3$, TMS): δ 141.7, 134.9, 131.3, 128.4, 127.9, 125.3 (aromatic and vinyl carbons), 57.1 (d, C(2)), 49.6, 46.6 (d, C(6), C(5)), 38.7, 37.4 (d, C(1), C(7)), 36.3 (t, CH_2Ph), 33.4 (t, C(10)), 29.6, 28.5 (t, C(9), C(8)) ppm.

3-(3-Phenylprop-1-en-1-yl)tricyclo[3.2.1.$0^{2,4}$]octane (V). Mass spectrum (60 eV): M^+ 224, *m/e* 170, 155, 133, 129, 105, 91, 79, 67; ^{1}H NMR (100 MHz, $CDCl_3$, TMS): δ 7.45—7.00 (m, 5H), 5.60 (dt, *J* 15 Hz, *J* 7 Hz, 1H), 4.90 (dd, *J* 15 Hz, *J* 8 Hz, 1H), 3.29 (d, *J* 7 Hz, 2H), 2.22 (m, 2H), 1.65—1.10

(m, 6H), 1.00—0.45 (m, 3H) ppm; ^{13}C NMR (25.2 MHz, $CDCl_3$, TMS): δ 140.7, 133.0, 128.2, 128.0, 126.1, 125.6 (aromatic and vinyl carbons), 38.9 (t, CH_2Ph), 35.8 (d, C(1), C(5)), 29.4 (t, C(6), C(7)), 28.3 (t, C(8)), 24.3 (d, C(2), C(4)), 16.7 (d, C(3)) ppm.

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