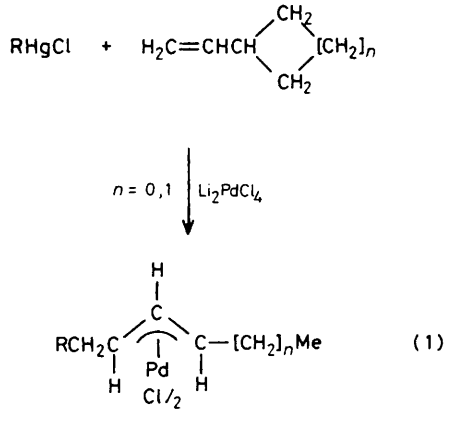
Synthesis, Stereochemistry, Mechanisms of Formation, and *X*-Ray Crystal Structures of Enantiomerically Pure π-Allylpalladium Compounds formed *via* Palladium-promoted Ring Opening of Bicyclic Alkenes

Richard C. Larock,*[a] Hanchul Song,[a] Sangsoo Kim,[b] and Robert A. Jacobson[b]

[a] *Department of Chemistry, Iowa State University, Ames, Iowa 50011, U.S.A.*
[b] *Department of Chemistry and Ames Laboratory—DOE, Iowa State University, Ames, Iowa 50011, U.S.A.*

The synthesis, stereochemistry, mechanisms of formation, and *X*-ray crystal structures of enantiomerically pure π-allylpalladium compounds (**1**)—(**3**) prepared by palladium hydride addition to (1*R*)-(+)-α-pinene, (1*S*)-(−)-α- or -β-pinene, and (1*S*)-(+)-2- or -3-carene respectively are presented.

Vinylcyclopropanes[1] and methylenecyclopropanes[2] have been ring-opened by palladium(0) reagents and palladium dichloride. We recently reported that the addition of hydrido- and organo-palladium compounds to alkenyl- and methylene-cyclopropanes and -cyclobutanes leads *via* ready ring-opening to high yields of π-allylpalladium compounds (equation 1).[3]

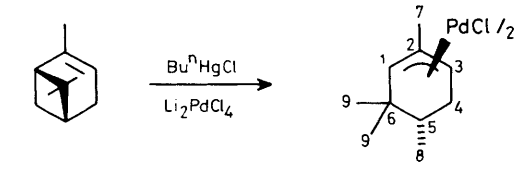


(1)

The mechanism we suggested for this process has recently been supported by the work of Fischetti and Heck.[4] We now report the synthesis, stereochemistry, further details of the mechanism of formation, and *X*-ray crystal structures of enantiomerically pure π-allylpalladium compounds formed by this process.

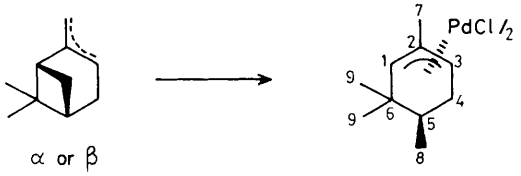
We elected to examine the stereochemistry of this process by studying the addition of a palladium hydride to 98—99% optically pure (1*R*)-(+)-α-pinene, (1*S*)-(−)-α-pinene, and (1*S*)-(−)-β-pinene (equations 2 and 3). These reactions provided π-allylpalladium compounds (**1**) {20% yield, $[\alpha]_D^{20}$ −73.2° ($CHCl_3$, 6.6 mg/ml)}† and (**2**) {(1*S*)-(−)-α-pinene: 20% yield, $[\alpha]_D^{20}$ +73.3° ($CHCl_3$, 6.7 mg/ml); (1*S*)-(−)-β-pinene: 71% yield, $[\alpha]_D^{20}$ +73.3° ($CHCl_3$, 11.66 mg/ml)} which

† Characterization for (**1**): m.p. 142 °C (decomp.); ^{1}H n.m.r. ($CDCl_3$) δ 0.67 (1 H, d, *J* 14.9 Hz, H-4), 0.75 (3 H, s, H-9), 0.78 (3 H, d, *J* 8.3 Hz, H-8), 1.20 (3 H, s, H-9), 1.98 (1 H, m, H-4), 2.01 (3 H, s, H-7), 2.80 (1 H, m, H-5), 4.50 (1 H, s, H-3), 4.74 (1 H, s, H-1); ^{13}C n.m.r. ($CDCl_3$) δ 15.3, 22.5, 22.7, 22.9, 34.4, 39.0, 41.4, 79.3, 90.9, 113.7; i.r. (neat) 2960, 2930, 2870, 2830, 1480, 1465, 1445, 1390, 1380, 1370, 1360, 1210, 900 cm^{-1}.



(2)

(1)



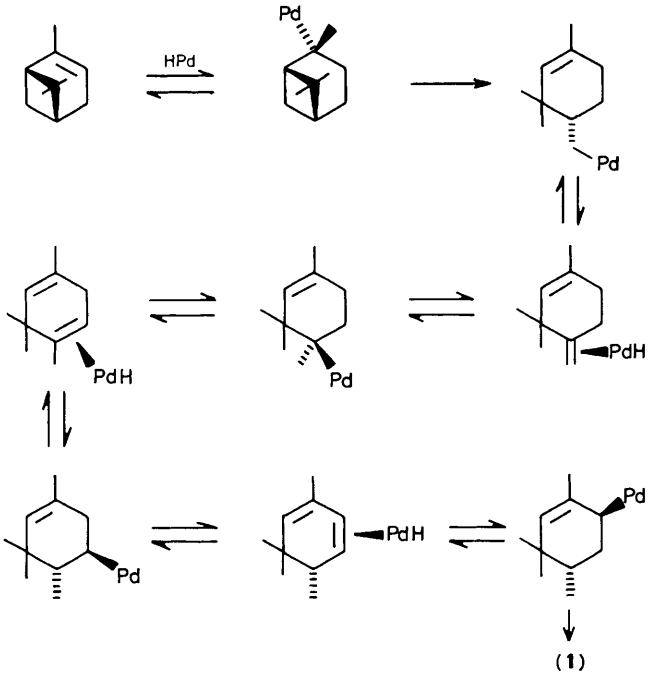
(3)

(2)

appear to be optically pure by comparison of the specific rotations obtained from both the (*R*) and the (*S*) enantiomers and by *X*-ray diffraction. This method appears to afford one of the few good ways presently available for the preparation of enantiomerically pure π-allylpalladium compounds.[1e,5,6]

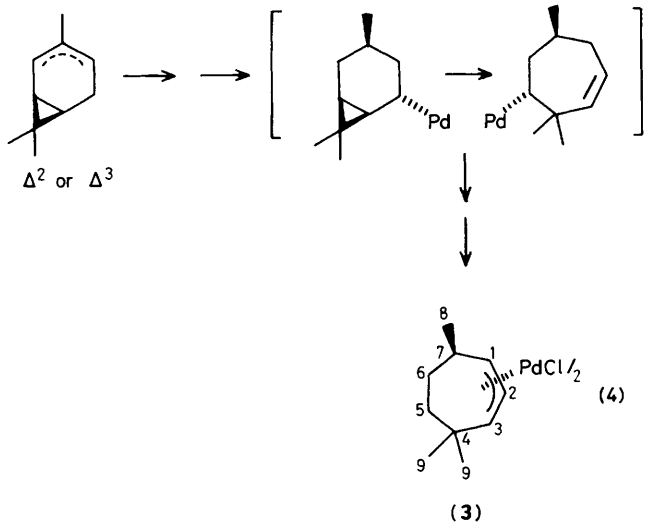
While α- and β-pinenes have previously been converted into π-allylpalladium compounds,[6] those reactions did not involve ring opening. The formation of compounds (**1**) and (**2**) is best explained mechanistically by a sequence involving stereospecific palladium hydride addition and elimination reactions and cyclobutylcarbinylpalladium ring opening (Scheme 1). The ring opening step apparently proceeds by *syn*-elimination of the palladium and methylene moieties facilitated by relief of strain in the four-membered ring.

The structure of compound (**2**) derived from β-pinene was established by *X*-ray crystallography and is shown in Figure 1.‡ The allyl groups adopt a *cis*-arrangement and the chlorine bridge is bent, the interplanar angle between Pd(1)–Cl(1)–Cl(2) and Pd(2)–Cl(1)–Cl(2) being 130.5°. While most dimeric



(1)

Scheme 1



(4)

(3)

halogen-bridged π-allylpalladium complexes adopt a '*trans*-planar' arrangement,[7] '*cis*-bent' features have been reported in a few cases,[8] only one of which is acyclic.[8c]

Analogous palladium hydride reactions have been carried out on (+)-2-carene (>97% purity) and (+)-3-carene (>99% purity) (equation 4). The former alkene afforded π-allylpalladium compound (**3**) in 19% yield, $[\alpha]_D^{20}$ −70.6° ($CHCl_3$, 7.24 mg/ml), while the latter alkene gave the same palladium compound in 23% yield, $[\alpha]_D^{20}$ −71.7° ($CHCl_3$, 7.14 mg/ml).§

‡ *Crystal data* for (**2**): $Pd_2Cl_2C_{20}H_{34}$, orthorhombic, space group $P2_12_12_1$, $Z = 4$, $a = 11.860(7)$, $b = 22.476(13)$, $c = 8.367(3)$ Å, $D_c = 1.663$ g/cm^3, $\mu = 18.15$ cm^{-1} (Mo-K_α, $\lambda = 0.71069$ Å, graphite-monochromated). The structure was solved by analysis of a Patterson superposition map and refined to $R = 0.026$ and $R_w = 0.034$ ($\omega = 1/\sigma_F^2$) against 1260 observed ($I \geq 3\sigma_I$) reflections ($2\theta \leq 50°$). The absolute configuration of the structure was established by Hamilton's significance test and a sensitivity test on 18 selected reflections.

Crystal data for (**3**): $Pd_2Cl_2C_{20}H_{34}$, monoclinic, space group $P2_1/n$, $Z = 2$, $a = 8.442(5)$, $b = 24.502(7)$, $c = 5.621(3)$ Å, $\beta = 101.42(6)°$, $U = 1139.8(9)$ Å^3, $D_c = 1.615$ g/cm^3, $\mu = 17.95$ cm^{-1} (Mo-K_α, $\lambda = 0.70966$ Å, graphite-monochromated). The structure was solved by the heavy atom method and refined with anisotropic temperature factors for the nonhydrogen atoms to $R = 0.041$ and $R_w = 0.041$ ($\omega = 1/\sigma_{F^2}$) against 1014 observed ($I \geq 3\sigma_I$) reflections ($2\theta \leq 50°$). Hydrogen atoms were included in the calculations, but not varied. Equally strong disorder peaks were observed at the positions of C(42) and C(72) in the electron density map. The subsequent occupancy refinements indicated half population of the positions. Also, the distance between C(5) and C(6) is shorter than that expected for a C–C single bond, and the thermal ellipsoids of these atoms are severely elongated out of the approximate plane of the seven-membered ring. The difference electron density map calculated without C(5) and C(6) showed 'banana-shaped' electron density around the positions. This suggests that the C(5)–C(6) bond undergoes a large amplitude of bending motion and the density represented in the diffraction data is a time-average of the motion. This interpretation is consistent with the n.m.r. spectroscopic results which do not support the presence of a double bond between C(5) and C(6).

Atomic co-ordinates, bond lengths and angles, and thermal parameters for both structures have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ Characterization for (**3**): m.p. 147—150 °C (decomp.); ^{1}H n.m.r. ($CDCl_3$) δ 1.05 (3 H, s, H-9), 1.10 (3 H, d, *J* 7.1 Hz, H-8), 1.32 (3 H, s, H-9), 1.38—1.48 (1 H, m, H-6), 1.56—1.69 (1 H, m, H-6), 1.82—1.97 (1 H, m, H-5), 2.09—2.28 (1 H, m, H-5), 4.59—4.78 (3 H, m, H-1, H-2, H-3); ^{13}C n.m.r. ($CDCl_3$) δ 23.6, 29.7, 30.0, 31.5, 38.9, 39.4, 39.6, 90.1, 95.0, 97.2; i.r. (neat) 2951, 2914, 2866, 1458, 754 cm^{-1}.

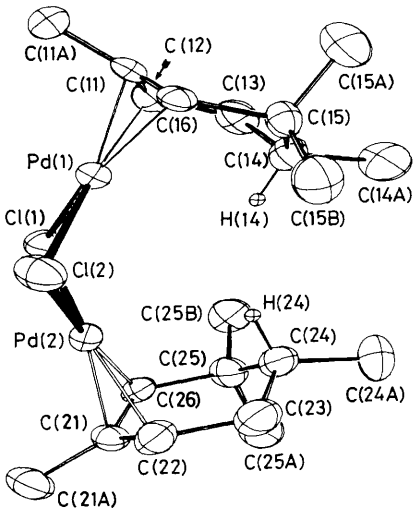


Figure 1. An ORTEP drawing of compound (**2**). Hydrogen atoms except H(14) and H(24) are omitted for clarity. Selected average distances and angles are: Pd–Cl 2.416, C–C(allyl) 1.393 Å; Cl–Pd–Cl 88.70°, Pd–Cl–Pd 81.03°, C–C–C(allyl) 114.8°; Pd–C(allyl) distances range from 2.061 to 2.161 Å.

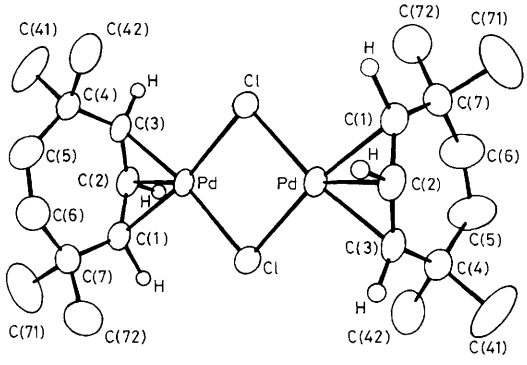


Figure 2. An ORTEP drawing of compound (**3**). Hydrogen atoms are omitted for clarity. Selected distances and angles are: avg. Pd–Cl 2.414, avg. Pd–C(allyl) 2.115, avg. C(allyl)–C(allyl) 1.411 Å; Cl–Pd–Cl 87.0, Pd–Cl–Pd 93.0, allylic C–C–C 123.5°.

The structure of compound (**3**) was established by *X*-ray crystallography and is shown in Figure 2.‡ The molecule resides at a crystallographic inversion point, adopting a '*trans*-planar' arrangement, in contrast to compound (**2**). The allylic C–C–C bond angle of 123.5(9)° is somewhat larger than that of compound (**2**) (114.8°).

It is noteworthy that the same π-allylpalladium compound is formed from both 2- and 3-carene. While the formation of compounds (**1**) and (**2**) can be explained by palladium hydride addition to the starting alkenes to form a tertiary alkylpalladium intermediate which can immediately undergo ring opening, the formation of compound (**3**) requires a palladium migration prior to ring opening. We believe that the alkylpalladium intermediates which actually undergo ring opening are determined by the conformations of the alkenes or their intermediate palladium hydride adducts leading up to ring opening.

These stereospecific rearrangements provide a novel route to enantiomerically pure π-allylpalladium compounds which should prove useful in mechanistic studies of the reactions of π-allylpalladium compounds.

We thank the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. The X-ray studies were supported by the Office of Basic Energy Sciences, Materials Science Division, Department of Energy. We also thank the National Institutes of Health for partial financial support and Johnson Matthey Inc. for generous loans of palladium chloride.

Received, 10th November 1986; Com. 1607

References

1 (a) Y. Morizawa, K. Oshima, and H. Nozaki, *Tetrahedron Lett.*, 1982, **23**, 2871; (b) G. P. Chiusoli, M. Costa, L. Pallini, and G. Terenghi, *Transition Met. Chem. (Weinheim, Ger.)*, 1982, **7**, 304; (c) A. D. Ketley and J. A. Braatz, *J. Organomet. Chem.*, 1967, **9**, P5; (d) T. Shono, T. Yoshimura, Y. Matsumura, and R. Oda, *J. Org. Chem.*, 1968, **33**, 876; (3) M. U. Ahmad, J.-E. Bäckvall, R. E. Nordberg, T. Norin, and S. Strömberg, *J. Chem. Soc., Chem. Commun.*, 1982, 321; (f) J.-E. Bäckvall and E. E. Björkman, *J. Chem. Soc., Chem. Commun.*, 1982, 693; (g) D. Wilhelm, J.-E. Bäckvall, R. E. Nordberg, and T. Norin, *Organometallics*, 1985, **4**, 1296.

2 (a) P. Binger and U. Schuchardt, *Chem. Ber.*, 1980, **113**, 1063, 3334; 1981, **114**, 3313; (b) P. Binger and A. Germer, *Chem. Ber.*, 1981, **114**, 3325; (c) P. Binger, M. Cetinkaya, M. J. Doyle, A. Germer, and U. Schuchardt in 'Fundamental Research in Homogeneous Catalysis,' vol. 3, ed. M. Tsutsui, Plenum, New York, 1979; (d) P. Binger and U. Schuchardt, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 249; (e) R. P. Hughes, D. E. Hunton, and K. Schumann, *J. Organomet. Chem.*, 1979, **169**, C37; (f) R. Noyori and H. Takaya, *Chem. Commun.*, 1969, 525; (g) B. K. Dallas and R. P. Hughes, *J. Organomet. Chem.*, 1980, **184**, C67; (h) M. Green and R. P. Hughes, *J. Chem. Soc., Chem. Commun.*, 1974, 686; (i) M. Green and R. P.Hughes, *J. Chem. Soc., Dalton Trans.*, 1976, 1880; (j) R. Goddard, M. Green, R. P. Hughes, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1976, 1890.

3 R. C. Larock and S. Varaprath, *J. Org. Chem.*, 1984, **49**, 3432.

4 W. Fischetti and R. F. Heck, *J. Organomet. Chem.*, 1985, **293**, 391.

5 (a) T. Hayashi, M. Konishi, and M. Kumada, *J. Chem. Soc., Chem. Commun.*, 1983, 736; (b) T. Hayashi, T. Hagihara, M. Konishi, and M. Kumada, *J. Am. Chem. Soc.*, 1983, **105**, 7767; (c) T. Hayashi, M. Konishi, and M. Kumada, *J. Chem. Soc., Chem. Commun.*, 1984, 107.

6 (a) B. M. Trost, P. E. Strege, L. Weber, T. J. Fullerton, and T. J. Dietsche, *J. Am. Chem. Soc.*, 1978, **100**, 3407; (b) T. Hosokawa, T. Uno, S. Inui, and S. Murahashi, *J. Am. Chem. Soc.*, 1981, **103**, 2318.

7 F. R. Hartley, 'The Chemistry of Platinum and Palladium,' Applied Science Publishers, Ltd., London, 1973, p. 424.

8 (a) B. T. Kilbourn, R. H. B. Mais, and P. G. Owston, *Chem. Commun.*, 1968, 1438; (b) J.-E. Bäckvall and E. E. Björkman, *J. Chem. Soc., Chem. Commun.*, 1982, 693; (c) G. R. Davies, R. H. B. Mais, S. O'Brien, and P. G. Owston, *Chem. Commun.*, 1967, 1151.