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Preliminary communication

CHLOROPALLADATION OF 7-METHYLENE-1-PHENYLBICYCLO[4.1.0]-HEPTANE: AN INTERMEDIATE CONTAINING CARBONIUM ION CHARACTER*

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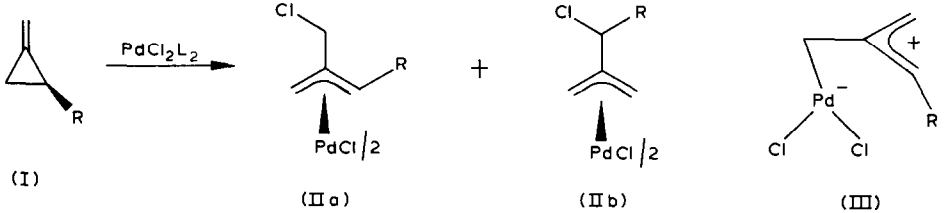
Summary

The chloropalladation of 7-methylene-1-phenylbicyclo[4.1.0]heptane in methanol, provides evidence for the intermediacy of an organopalladium species with carbonium ion character in the cyclopropane ring opening.

Recently, the mechanism of the chloropalladation of alkyl- and aryl-substituted methylenecyclopropanes (I) has been theoretically and experimentally investigated [1,2]. It was proposed that the π-allylpalladium complexes IIa and IIb (Scheme 1) result from the suprafacial addition of Pd—Cl to a cyclopropane opening in a disrotatory fashion. Although theory predicts that chloride transfer should require little additional activation energy, the point at which this occurs could not be determined. However, the zwitterionic species III was eliminated as a possible intermediate. This communication presents evidence for the intermediacy of a species with significant carbonium ion character in the ring opening of 7-methylene-1-phenylbicyclo[4.1.0]heptane (IV) [3,4].



(I) (IIa) (IIb) (III)

SCHEME 1

*Work initiated at Wesleyan University, Middletown, CT.

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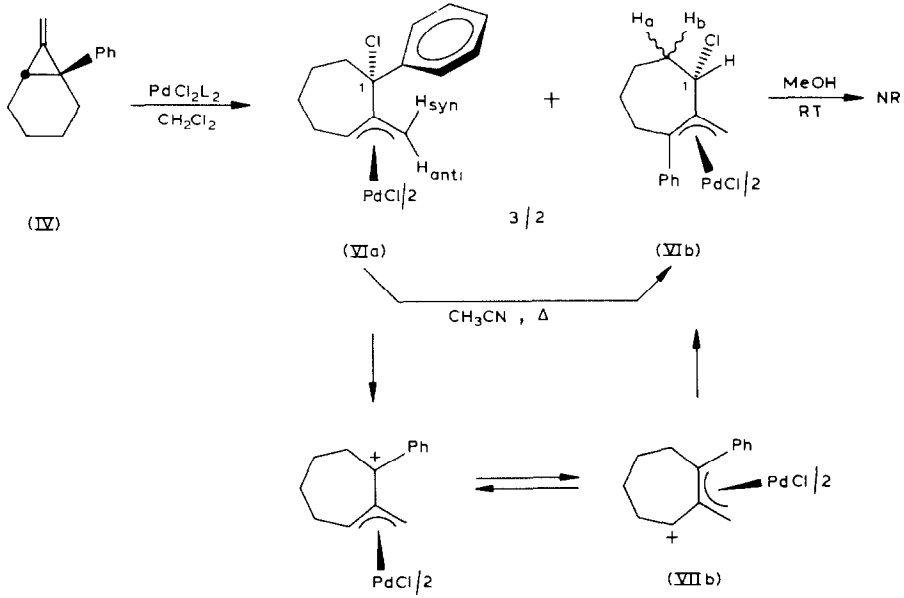
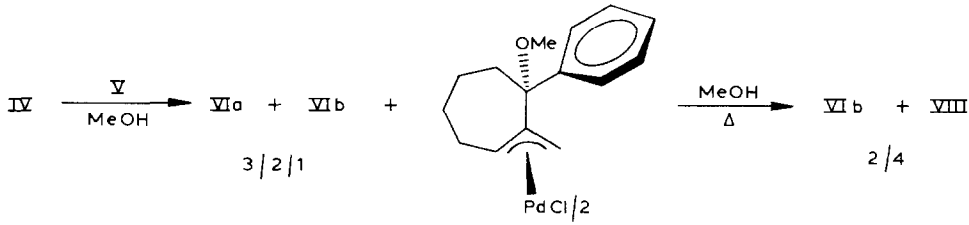
The reaction of bis(acetonitrile)palladium chloride (V) with IV (CH_2Cl_2, 23°C, 20 min) afforded a mixture of palladium allyls VIa [3,5] and VIb [3,6] (3/2 by ^{1}H NMR integration, 96% yield, Scheme 2). The conformation for VIa at C(1) (Cl-ax., Ph-eq.) was assigned from ^{1}H NMR spectroscopy; the resonance signals for H_{syn} and H_{anti} for VIa are 1.0 and 0.5 ppm upfield from the respective signals for VIb due to the shielding effects of the phenyl ring current. The conformation for VIb at C(1) (Cl-ax., H-eq.) was assigned from the vicinal coupling to H_a and H_b (2.4 and 5.8 Hz).



SCHEME 2

The kinetically controlled product mixture VIa/VIb, 3/2, could be completely converted into the minor isomer VIb (CH_3CN, 82°C, 24 h, 99% yield). The interconversion of VIa into VIb involves ionization of the axial chloride to afford an η^3-cationic trimethylenemethane (VIIa), in equilibrium with VIIb via migration about the trimethylenemethane [2,7]. Axial attack of chloride on VIIb affords the product VIb (Scheme 2).

The reaction of IV with V (CH_3OH, 23°C, 20 min) afforded a mixture of VIa, VIb and VIII [3,8] (3/2/1 by ^{1}H NMR integration, 94% yield) (Scheme 3).



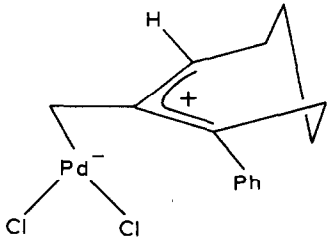
SCHEME 3

(VIII)

The conformation of VIII at C(1) (OMe-ax., Ph-eq.) was assigned by comparison of the resonance signals for H_{syn} and H_{anti} with those of VIa. The mixture of VIa/VIb/VIII, 3/2/1, could be converted into a mixture of VIb and VIII (1/2 by ^1H NMR integration, CH_3OH, 65°C, 24 h, 98% yield). The complete conversion of VIa into VIII presumably occurs via axial chloride ionization to VIIa followed by rapid, irreversible trapping by methanol [2]. The isomeric mixture VIa/VIb, 3/2 did not react in methanol (23°C, 24 h) to afford VIII (Scheme 2). Thus, the methoxy-substituted allyl VIII formed in the reaction of IV and V in methanol (23°C) (Scheme 3) can not be present due to solvolysis of VIa. The identical ratio of VIa/VIb for reaction in both CH_3OH and CH_2Cl_2 further supports this fact.

The product VIII, therefore, must result from competitive addition of palladium and methanol across the cyclopropane ring in either a *cis* fashion or by nucleophilic attack of methanol on an intermediate organopalladium species in a *trans* fashion. To our knowledge only clear examples of *trans*-alkoxypalladation have been reported [9,10]. The regiospecific addition of methanol to the phenyl-substituted cyclopropane carbon of IV strongly implies that the intermediate in the ring opening should involve some carbonium ion character. An extreme form of this intermediate might plausibly be represented by the zwitterionic species IX. This type of intermediate had been previously proposed [13,14] and was later eliminated [1,2] for the chloropalladation (in CH_3OH) of dialkyl- and phenyl-substituted methylenecyclopropanes due to the absence of any methoxy-substituted product.

We are currently investigating the extent to which the intermediate resembles the zwitterionic species IX as well as the application of VIb to organic synthesis.



(IX)

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References

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2 B.K. Dallas, R.P. Hughes, and K. Schumann, J. Am. Chem. Soc., 104 (1982) 5380.
3 Satisfactory microanalytical data obtained for this compound.

4 Prepared from 1-phenylcyclohexene (65% yield) in a manner similar to S. Arora and P. Binger, Synthesis, (1974) 801.
IV: b.p. 39—40°C, 0.025 mmHg; ^{1}H NMR ($CDCl_3$) δ 7.1—7.4 (m, 5H, Ph), 5.5 (m, 2H, C=CH_2), 1.2—2.2 (m, 9H, C-H) ppm; IR (neet) 1600m, 1480m, 880s, 760s, 690s cm^{-1}.

5 VIa could be obtained from the mixture by fractional crystallization (CH_2Cl_2/hexanes). VIa: m.p. 158°C (dec.); ^{1}H NMR ($CDCl_3$) δ 7.2—8.0 (m, 5H, Ph), 3.75 (d, 1H, *J* 5.6 Hz, H-allyl), 2.92 (s, 1H, H_{syn}), 2.52 (s, 1H, H_{anti}), 1.0—2.5 (m, 8H, CH_2) ppm.

6 VIb: m.p. 185°C (dec.); ^{1}H NMR ($CDCl_3$) δ 7.1—7.6 (m, 5H, PH), 4.87 (dd, 1H, *J* 2.4, 5.8 Hz, *CH*Cl), 3.93 (s, 1H, H_{syn}), 3.02 (s, 1H, H_{anti}), 1.2—2.6 (m, 8H, CH_2) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 142.93, 128.94, 128.33, 127.35, 121.27, 98.62, 64.25, 63.44, 40.18, 37.67, 26.92, 24.98 ppm.

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8 VIII could be obtained from the mixture by fractional crystallization (CH_2Cl_2/hexanes). VIII: m.p. 190°C (dec.); ^{1}H NMR ($CDCl_3$) δ 7.1—8.0 (m, 5H, Ph), 3.81 (d, 1H, *J* 5.6 Hz, H-allyl), 3.28 (s, 3H, OMe), 3.02 (s, 1H, H_{syn}), 2.62 (s, 1H, H_{anti}), 1.0—2.5 (m, 8H, CH_2) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 142.45, 129.28, 128.25, 127.39, 126.90, 84.46, 82.63, 63.23, 52.20, 30.36, 29.80, 27.77, 24.15 ppm.

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10 Although the product VIII reflects apparent *trans*-addition, the *cis*-addition of Pd—OCH_3 can not be eliminated as certain (1-methylenecycloalkyl)palladium chloride dimers are presumed to undergo rapid η^3 to η^1 to η^3 isomerization in solution [1,11,12]. Experiments to determine the stereochemistry of addition are in progress.

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