*Journal of Organometallic Chemistry*, 330 (1987) C33–C36
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

**Preliminary communication**

# Catalytic carbopalladation of ω-methylenebicyclo[*n*.1.0]alkanes

**William A. Donaldson* and Christine A. Brodt**

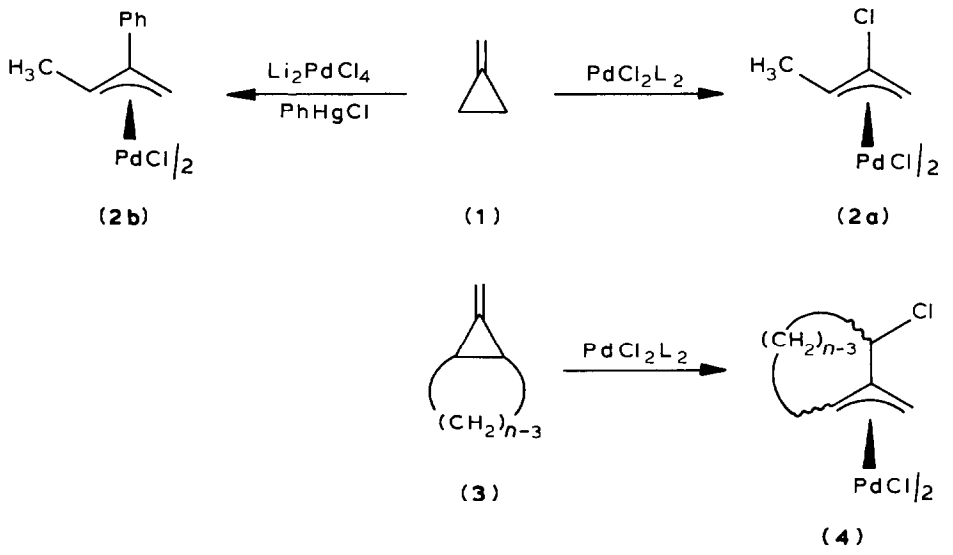
*Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53233 (U.S.A.)*

(Received May 4th, 1987)

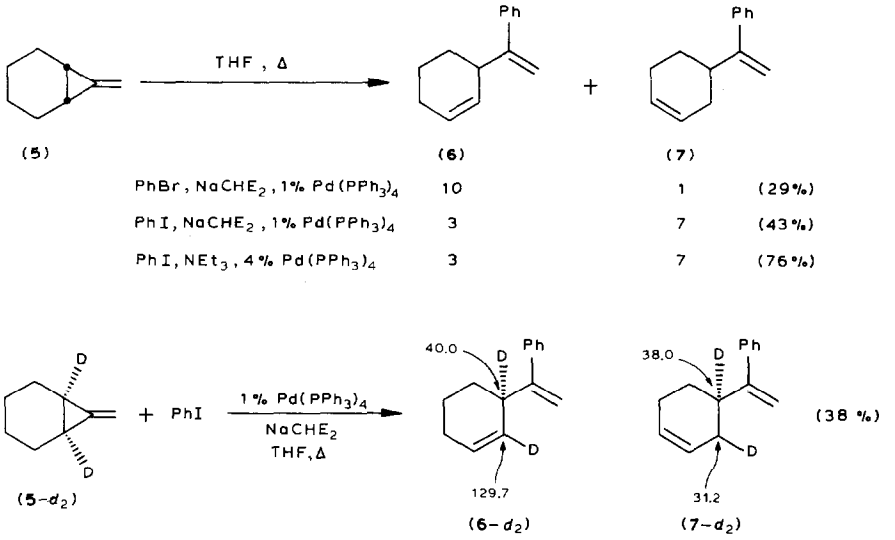
## Abstract

ω-Methylenebicyclo[*n*.1.0]alkanes undergo carbopalladation via cleavage of the C(1)–C(2) cyclopropane bond. The resultant σ-butenyl complexes decompose via β-hydride elimination to afford the 1-cycloalkenylstyrene products.

The reactivity of strained organic rings with transition metals is an area of intense research activity [1]. The chloropalladation [2] and carbopalladation [3] of methylenecyclopropane (**1**) have been reported to proceed via C(1)–C(2) cleavage to yield the (2-substituted-crotyl)palladium chloride dimers (**2**). In contrast, the chloropalladation of ω-methylenebicyclo[*n*.1.0]alkanes (**3**) occurs by cleavage of the C(2)–C(3) cyclopropane bond to afford the (3-chloro-2-methylenecycloalkyl)palladium chloride dimers (**4**) [4,5]. We have investigated the reactivity of complexes **4**




0022-328X/87/$03.50 




as part of a ring homologation–functionalization methodology [6]. Unfortunately the chloropalladation–nucleophilic addition sequence cannot be rendered catalytic with typical palladium(0) oxidants. Thus we were keenly interested in a recent report on the catalytic carbopalladation–nucleophilic addition reaction of the parent methylenecyclopropane (**1**) [7]. We herein report on the reactivity of substrates **3** under similar conditions.

Reaction of 7-methylenebicyclo[4.1.0]heptane (**5**) with bromo- or iodo-benzene and sodium diethylmalonate in the presence of $Pd(PPh_3)_4$ (0.01 equiv., THF, 60 °C, **5**–**7***d*) gave mixtures of 1-(3-cyclohexenyl)styrene (**6**) * and 1-(4-cyclohexenyl)styrene (**7**) ** as well as recovered diethylmalonate. Similarly, the reaction of **5**-$d_2$ *** under the above reaction conditions gave 1-(2,3-dideutero-3-cyclohexenyl)styrene (**6**-$d_2$) and 1-(3,4-dideutero-4-cyclohexenyl)styrene (**7**-$d_2$). The location of deuterium label was confirmed by $^{13}C$ NMR spectroscopy. Use of triethylamine (3 equiv.) instead of sodium diethylmalonate improved the overall yield but did not effect the **6**/**7** product ratio ****.

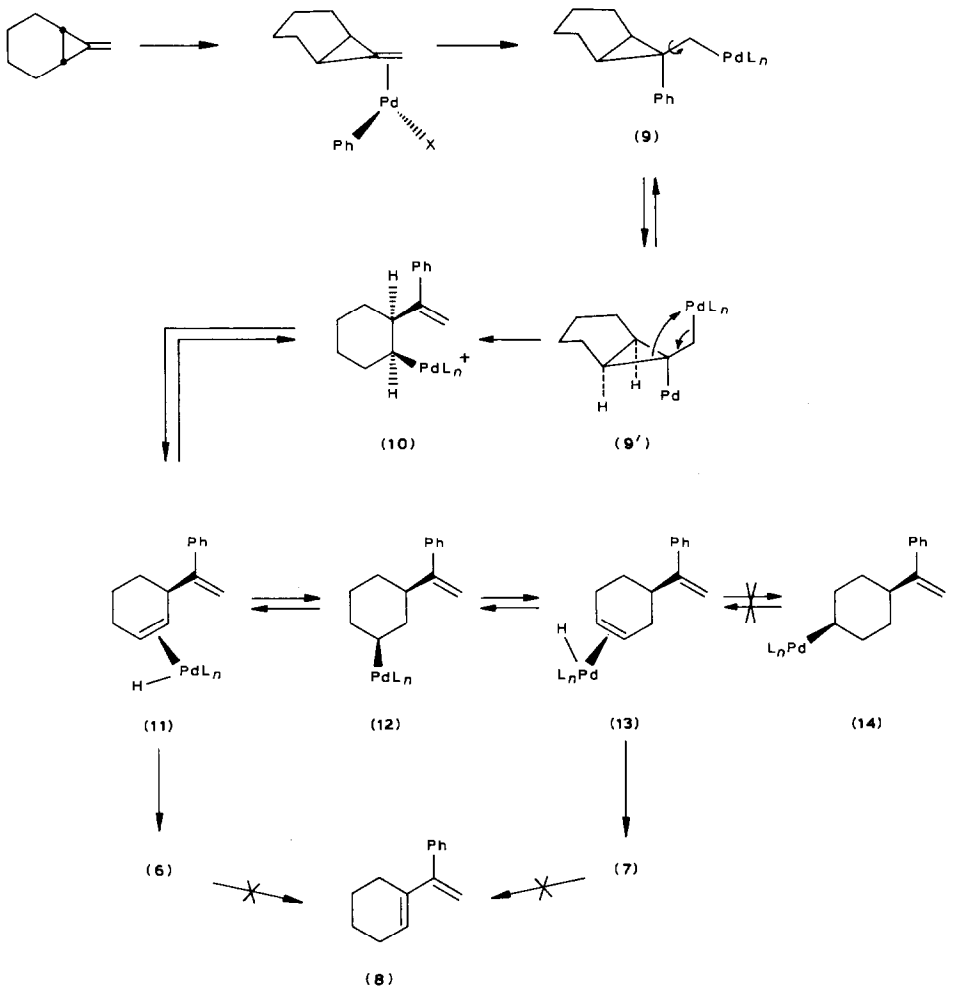
---

* This compound was identified by comparison to literature spectral data [8] as well as by comparison to the authentic $^1H$ NMR spectrum graciously provided by Prof. M. Gaudemar. **6**: 60 MHz $^1H$ NMR ($CDCl_3$) $\delta$ 7.3–7.0 (m, 5H), 5.66 (m, 2H), 5.18 (d, $J$ 1.5 Hz, 1H), 4.95 (m, 1H), 3.25 (brs, 1H), 2.1–1.4 (m, 6H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ 152.5, 129.7, 128.2, 127.1, 126.5, 126.0, 113.0, 40.0, 28.5, 25.2, 20.4 ppm.

** This compound was identified by comparison to an authentic sample prepared by Wittig olefination of 4-cyclohexenyl phenyl ketone [9]. **7**: $^1H$ NMR ($CCl_4$) $\delta$ 7.4–7.0 (m, 5H), 5.6 (brs, 2H), 5.10 (s, 1H), 4.95 (narrow multiplet, 1H), 2.7 (m, 1H), 2.0 (m, 4H), 2.0–1.2 (m, 2H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ 154.1, 142.7, 131.7, 128.6, 128.1, 127.0, 126.7, 110.7, 38.5, 31.6, 28.2, 25.8 ppm.

*** The deuterated material was prepared by the reaction of **5** with potassium butoxide in DMSO-$d_6$ (60 °C, 15 min) [4] and was shown to contain ~75% **5**-$d_2$ and ~15% **5**-$d_1$ based on GC/MS analysis.

**** Notably, isomerization of the products **6** or **7** to the more thermodynamically stable conjugated 1-(1-cyclohexenyl)styrene (**8**) is not observed. This compound was also independently prepared by Wittig olefination of 2-cyclohexenyl phenyl ketone. **8**: $^1H$ NMR ($CCl_3$) $\delta$ 7.3–7.1 (s, 5H), 5.56 (m, 1H), 5.10 (s, 1H), 4.89 (s, 1H), 2.3–1.5 (m, 8H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ 151.7, 142.1, 137.1, 129.1, 128.5, 127.9, 110.9, 26.4, 25.9, 22.9, 22.2 ppm.



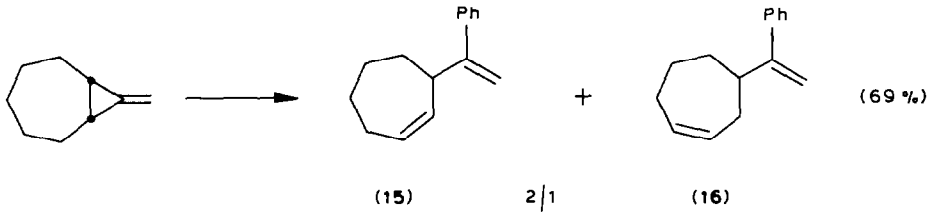

Scheme 1

We propose the mechanism shown in Scheme 1. Initial oxidative addition of the halobenzene generates an arylpalladium species which coordinates to the least hindered face of **5**. Olefin insertion generates the σ-cyclopropylcarbinylpalladium complex **9** which may undergo relatively free C–C bond rotation. In rotomer **9′** the σ-cyclopropylcarbinylpalladium complex may rearrange to the σ-homoallyl palladium complex **10** [10 *]. The σ-homoallyl complex **10** can only undergo *syn*-β-hydride elimination to afford the (olefin)palladium hydride **11**. Loss of the ligand generates the product **6**, while olefin insertion into the Pd–H bond generates the σ-complex**12**. β-Hydride elimination of **12** may afford either **11** or the isomeric **13**. Loss of the olefin ligand from **13** would give rise to **7**. Palladium hydride complex **13** is not anticipated to undergo olefin insertion to afford σ-complex **14** since the

* Reference number with asterisk indicates a note in the list of references.

resultant *cis*-1,4-disubstituted cyclohexane would require one substituent in a sterically unfavorable axial position.

In a similar fashion ω-methylenebicyclo[5.1.0]octane reacts with iodobenzene in the presence of $Pd(PPh_3)_4$ (0.02 molar equiv.) and sodium diethylmalonate to yield **15** and **16** *.




In summary, ω-methylenebicyclo[*n*.1.0]alkanes undergo catalytic carbopalladation via C(1)–C(2) bond cleavage. This is in direct contrast to the C(2)–C(3) cleavage which occurs during the chloropalladation of these same substrates. We are currently investigating the origin of this difference in reactivity.

**Acknowledgments.** The authors are grateful to the Donors of the Petroleum Research Fund, (No. 18822-AC1), administered by the American Chemical Society, and to Marquette University for financial support. Generous donations of palladium chloride from Johnson–Matthey, Inc. are acknowledged. We are indebted to Professor M. Gaudemar for a $^1H$ NMR spectrum of compound **6**.

## References

1 P. Binger and H.M. Büch, Top. Curr. Chem., 135 (1987) 77.
2 R. Noyori and H. Takaya, J. Chem. Soc., Chem. Comm., (1969) 525.
3 R.C. Larock and S. Varaprath, J. Org. Chem., 49 (1984) 3432.
4 T.A. Albright, P.R. Clemens, R.P. Hughes, D.E. Hunton and L.D. Margerum, J. Am. Chem. Soc., 104 (1982) 5369; R.P. Hughes, D.E. Hunton and K. Schumann, J. Organomet. Chem., 184 (1980) C67.
5 W.A. Donaldson, Organometallics, 5 (1986) 223; W.A. Donaldson, J. Organomet. Chem., 269 (1984) C25.
6 W.A. Donaldson and V.J. Grief, Tetrahedron Lett., (1986) 2345; W.A. Donaldson and B.S. Taylor, ibid., (1985) 4163.
7 G. Balme, G. Fournet and J. Gore, Tetrahedron Lett., (1986) 3855.
8 M. Bellassoued, Y. Frangin and M. Gaudemar, Synthesis, (1977) 205.
9 J.M. Andreev, G.P. Kugatova-Shemyakina and L.S. Anarkulova, Biol. Aktiv. Soedin., (1968) 79.
10 A similar mechanism has been proposed for the arylpalladation of **1** [3], and for the chloropalladation of 2,3-dicarbomethoxymethylenecyclopropane [11].
11 M. Green and R.P. Hughes, J. Chem. Soc., Dalton Trans., (1976) 1880.

* **15**: $^{13}C\{^1H\}$ NMR ($CDCl_3$, partial) δ 153.2, 112.3, 45.5, 33.0, 29.6, 28.7, 27.1 ppm; **16**: $^{13}C\{^1H\}$ NMR ($CDCl_3$, partial) δ 155.7, 110.7, 42.7, 38.4, 34.9, 28.7, 26.8 ppm.