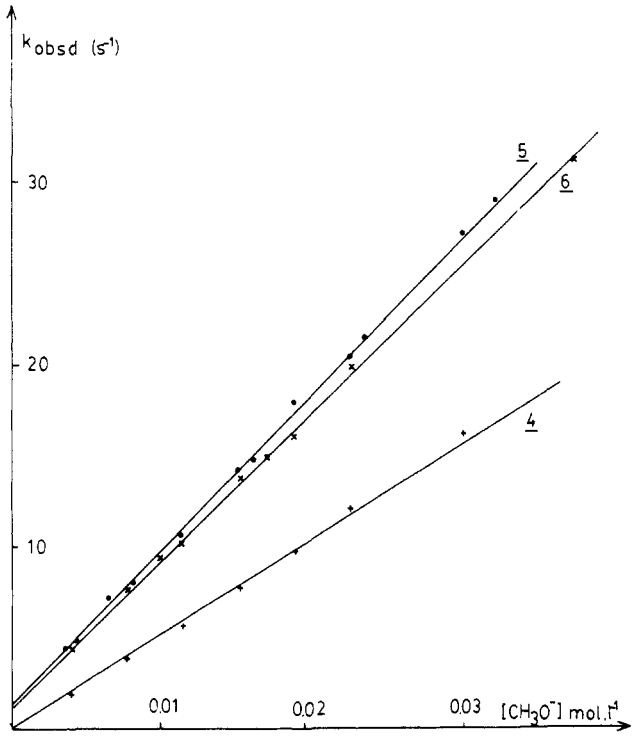


Figure 2. The methoxide ion concentration dependence of k_{obsd} (s^{-1}) for the ionization of the $Cr(CO)_3$ carbon acids **4**, **5**, and **6** in 98:2 Me_2SO–MeOH (t = 25 °C).

a deuterium content greater than 97% d_2 (which was evaluated from a 250-MHz proton NMR spectrum). The product was recrystallized from CH_2Cl_2–hexane to yield yellow crystals, mp 159 °C. All the kinetic experiments carried out with **5**-d_2 in the stopped-flow apparatus did not reveal any relaxation effect ascribable to the deprotonation of a hydrogen compound, further confirming the isotopic purity of **5**-d_2.

Solvents were purified and solutions made up as previously described.[42]

Measurements. Kinetic studies were carried out by using a Durrum stopped-flow spectrophotometer, with a thermostated cell compartment (±0.2 °C). All experiments were performed under first-order conditions, with a large excess of the base (10^{-3}–0.2 M) over the substrate concentration ((~3–5) × 10^{-5} M). Under these experimental conditions, the observed first-order rate constant, k_{obsd}, for the approach to equilibrium

$$R_1R_2R_3CH + MeO^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_1R_2R_3C^- + MeOH$$

is simply given by

$$k_{obsd} = k_{-1} + k_1[MeO^-]$$

Plots of k_{obsd} vs. [MeO^-] were linear, as shown in Figure 2. This allowed determination of the rate constants k_1 and k_{-1} from slopes and intercepts, respectively. In some instances, the intercepts were too small to be accurately determined so that only the k_1 values could be obtained. The values of the equilibrium constants $K_1 = k_1/k_{-1}$ were calculated from the rate data obtained. The rate constants given in Tables I and II are considered accurate to ±5%.

The methoxide ion concentration dependence of k_{obsd} (s^{-1}) for the ionization of the $Cr(CO)_3$ carbon acids **4**–**6** in 98:2 Me_2SO–MeOH (t = 25 °C) is shown in Figure 2.

Acknowledgment. This word was completed during a period of sabbatical leave (P.G.F., Mc Gill University, Montreal, Canada) at ENSCP, and the provision of facilities etc. there is gratefully acknowledged.

Registry No. **1**, 21112-02-7; **2**, 1817-74-9; **3**, 1817-77-2; **4**, 73016-87-2; **5**, 32823-67-9; **6**, 32825-32-4.

(42) See, e.g., C. F. Bernasconi and F. Terrier, *J. Am. Chem. Soc.*, **97**, 7458–7466 (1975).

Stereochemistry and Mechanism of Palladium(II)-Induced Ring Opening of the Cyclopropane in a Vinylcyclopropane. Chloro- and Oxypalladation of (+)-2-Carene

Didier Wilhelm, Jan-E. Bäckvall,* Ruth E. Nordberg, and Torbjörn Norin

Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden

Received November 26, 1984

Reaction of (+)-2-carene (**1**) with $PdCl_2(MeCN)_2$ in a nonnucleophilic solvent such as chloroform or benzene resulted in a chloropalladation across the cyclopropane ring. The corresponding reaction performed in methanol or acetic acid gave a methoxy- and acetoxypalladation, respectively, across the cyclopropane ring. The chloropalladation showed a remarkable solvent dependence. Reaction in chloroform containing 2% of ethanol afforded mainly the six-membered ring (π-allyl)palladium complex **2** (**2**/**3** = 6.4:1), whereas reaction in benzene predominantly gave the seven-membered ring complex **3** (**2**/**3** = 1:6.1). Stereochemical studies showed that the ring opening by palladium has occurred with inversion for **1** → **2** but with retention for **1** → **3**, resulting in an overall trans chloropalladation in the latter case. The transformation of **1** to the methoxy and acetoxy complexes **5** and **7** occurred with the same stereochemistry as **1** → **2** (inversion). The (π-allyl)palladium complexes **2** and **7** were transformed to neomenthol (**12**) and α-terpineol (**14**), respectively.

Introduction

The activation of cyclopropanes by transition metals is an important type of reaction that has attracted considerable interest.[1-8] Two principal mechanisms for the activation, that result in opening of the ring, are possible. For example, the reaction may involve oxidative addition

(1) (a) Bishop, K. C. *Chem. Rev.* **1976**, *76*, 461. (b) Sarel, S. *Acc. Chem. Res.* **1978**, *11*, 204.

(2) (a) Tulip, T. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4201. (b) Rajaram, J.; Ibers, J. A. *Ibid.* **1978**, *100*, 829. (c) McQuillin, F. J.; Powell, K. G. *J. Chem. Soc., Dalton Trans.* **1972**, 2123. (d) *Ibid.* **1972**, 2129. (e) Salomon, R. G. *J. Chem. Soc., Chem. Commun.* **1976**, 89.

0276-7333/85/2304-1296$01.50/0

Scheme I

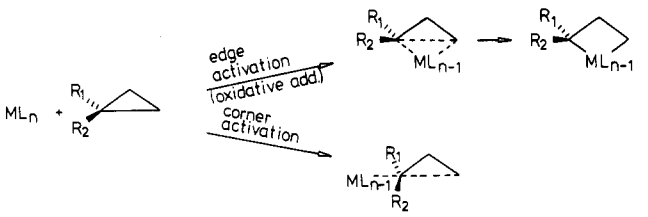


Table I. Chloropalladation of (+)-2-Carene[a]

entry	solv	% EtOH added	2	3	4	ratio of 2/3
1	benzene[b]	0	14	86		1:6.1
2	$CDCl_3$	0	58	42		1.4:1
3	$CHCl_3$[b,c]	0.6–1	71	21	8	3.4:1
4	$CHCl_3$	1	73	19	9	3.8:1
5		2	77	12	12	6.4:1
6		2.9	74	12	14	6.2:1
7		4	71	12	18	5.9:1
8		5	65	12	23	5.4:1

[a] Except for entries 1 and 3 the reactions were performed in an NMR tube and followed by ^1H NMR. The reactions were almost completed after 2 h, and the ratios did not change during the reaction. [b] The ratios in these cases were determined by ^1H NMR on the crude product. [c] Analytical grade chloroform ("pro analysi", FLUKA AG) was used.

of a carbon–carbon bond to the metal to give a metallacyclobutane (Scheme I), which in fact has been isolated in a few cases.[2a,b,3,4] Another principal pathway involves a corner activation by the metal (Scheme I). The stereochemical consequences of these two pathways are different. Thus, the cleavage of the carbon–carbon bond will take place with retention at carbon in the former case but with inversion at carbon in the latter.

If the cyclopropane activation by the metal takes place in the presence of a nucleophile, an addition similar to that occurring with olefins may take place. For example, oxymercuration of cyclopropanes is well established.[9] Such additions to cyclopropanes are also known for transition metals, and in particular chloropalladation of cyclopropanes has been studied.[5–8] Vinylcyclopropanes are known to react with palladium chloride to give π-allyl complexes via a chloropalladation reaction.[6,7] Since vinylcyclopropanes have similarities with conjugated dienes, some interesting mechanistic aspects arises. There are two

Table II

compd	isolated yield,[a] %	$[\alpha]^{20}_D$, deg	mp, °C
2	62	+130.2[b]	148–150[d,e]
3	51	+164.7[b]	144–146[d,f]
5	67	+124.7[c]	116–118[d,g]
7	38	+94.1[c]	71–73[g]

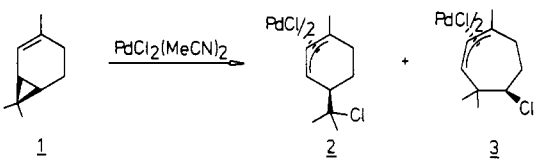
[a] Isolated yield of pure compounds (^1H NMR, ^{13}C NMR, IR, and elemental analysis: see Experimental Section) from chloro- or oxypalladation of 1, after column chromatography (silica). [b] In tetrahydrofuran. [c] In chloroform. [d] Decomposition. [e] Recrystallization from dichloromethane–hexane. [f] Recrystallization from chloroform–hexane. [g] Recrystallization from ether–pentane.

questions to be answered: (i) how is the ring activated by the metal (Scheme I) and (ii) what is the overall stereochemistry of the chloropalladation?

We have previously communicated our results on the stereochemistry of the chloropalladation of (+)-2-carene.[7] In this account we give full details of our preliminary results, report additional work on oxypalladation of (+)-2-carene, discuss the mechanism of these reactions, and finally describe some organic transformations of (+)-2-carene via the chloro- and oxypalladation reactions.

Results

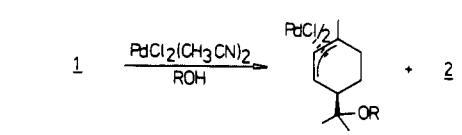
Chloro- and Oxypalladation. The reaction of (+)-2-carene (1) with $PdCl_2(MeCN)_2$ in different solvents was studied. When the reaction was performed in nonnucleophilic solvents such as chloroform, methylene chloride, or benzene, a chloropalladation takes place with the formation of (π-allyl)palladium complexes 2 and 3 (eq 1).



1 2 3 (1)

The ratio of the complexes 2 and 3 is strongly dependent on the solvent used (Table I). For example, reaction of $PdCl_2(MeCN)_2$ with 1 in benzene resulted in selective cleavage of the 1–6 bond and formation of 2 and 3 in a ratio of 1:6.1 (entry 1). On the other hand, when the reaction was performed in chloroform, the 1–7 bond is selectively cleaved and now 2 and 3 are formed in a ratio of 6.4:1.

As shown in Table I, small amounts of ethanol have a remarkable effect on the chloropalladation of 1 in chloroform. We discovered this unusual effect in product selectivity when we tried to repeat the chloropalladation reaction in the NMR tube. Chloropalladation of 1 in commercial chloroform (analytical grade) gave 2 and 3 in a ratio of 3.4:1, but reaction in deuteriochloroform afforded 2 and 3 in a ratio of 1.4:1! It occurred to us that commercial chloroform is stabilized with ethanol and on addition of ethanol to the deuteriochloroform reactions the selectivity for 2 increased (Table I). When ethanol is increased above 3%, the ethoxy adduct 4 starts to form in a considerable amount. The latter product is formed via an oxypalladation of 1 (eq 2).



(2)

4 R=C_2H_5
5 R=CH_3
6 R=cyclohexyl
7 R=$COCH_3$

(3) (a) Tipper, C. F. H. *J. Chem. Soc.* **1955**, 2045. (b) Hall, P. W.; Puddephatt, R. J.; Tipper, C. F. H. *J. Organomet. Chem.* **1974**, *71*, 145. (c) Puddephatt, R. J.; Quyser, M. A.; Tipper, C. F. H. *J. Chem. Soc., Chem. Commun.* **1979**, 626. (d) Al-Essa, R. J.; Puddephatt, R. J.; Quyser, M. A.; Tipper, C. F. H. *J. Am. Chem. Soc.* **1979**, *101*, 364. (e) Al-Essa, R. J.; Puddephatt, R. J.; Thompsom, P. J.; Tipper, C. F. H. *Ibid.* **1980**, *102*, 7546.

(4) Dominelli, N.; Oehlschlager, A. C. *Can. J. Chem.* **1977**, *55*, 364.

(5) (a) Albelo, G.; Rettig, M. F. *J. Organomet. Chem.* **1972**, *42*, 183. (b) Albelo, G.; Rettig, M. F. *J. Am. Chem. Soc.* **1975**, *97*, 4510. (c) Rettig, M. F.; Wilcox, D. E.; Fleischer, R. S. *J. Organomet. Chem.* **1981**, *214*, 261. (d) Parra-Hake, M.; Rettig, M. F.; Wing, R. M.; Woolcock, J. C. *Organometallics* **1982**, *1*, 1478.

(6) (a) Ketley, A. D.; Braatz, J. A. *J. Organomet. Chem.* **1967**, *9*, P5. (b) Shono, T.; Yoshimura, T.; Matsumura, Y.; Oda, R. *J. Org. Chem.* **1968**, *33*, 876.

(7) (a) Ahmad, M.; Bäckvall, J. E.; Nordberg, R. E.; Norin, T.; Strömberg, S. *J. Chem. Soc., Chem. Commun.* **1982**, 321. (b) Bäckvall, J. E.; Björkman, E. E. *Ibid.* **1982**, 693.

(8) (a) Green, M.; Hughes, R. P. *J. Chem. Soc., Dalton Trans.* **1976**, 1880. (b) Albright, T. A.; Clemens, P. R.; Hughes, R. P.; Hunton, D. E.; Margerum, L. D. *J. Am. Chem. Soc.* **1982**, *104*, 5369. (c) Dallas, B. K.; Hughes, R. P.; Schumann, K. *Ibid.* **1982**, *104*, 5380. (d) Binger, P.; Schuchhardt, U. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 249.

(9) (a) DePuy, C. H.; McGirk, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 1121. (b) DePuy, C. H. *Top. Curr. Chem.* **1973**, *40*, 73. (c) Bandaev, S. G.; Shabarov, Yu. S.; Hantschmann, A.; Weissenfels, M. *J. Prakt. Chem.* **1980**, *322*, 643. (d) Sokolov, V. I.; Rodina, N. B.; Reutov, O. A. *Zh. Org. Chim.* **1970**, *6*, 888.

Table III. ^{1}H NMR ($CDCl_3$) for (π-Allyl)palladium Complexes 2, 4, 5, and 7 (Figure 1)

complex	X	chem shifts δ: CH_3 (s)	H^2 (d)	H^3 (br d)	H^4 (m)	H^{6e} (m)	H^{6a} (m)	H^{5e} (m)	H^{5a} (m)	coupling const
2, X = Cl		1.67 1.54 1.50	5.36	4.94	1.74	1.92	2.3–2.0		0.92	see *a*
4, X = CH_2CH_3	3.60 (m) 3.35 (m) 1.16 (t)	1.48 1.13 1.08	5.33	5.04	1.55–1.35	1.87	2.3–1.98		0.72	as in *a* but $J_{6a,6e}$ = 18 Hz
5, X = OCH_3	3.26 (s)	1.48 1.14 1.08	5.34	5.02	1.6–1.4	1.87	2.28–1.97		0.72	as in *a* but $J_{4,5e}$ = 5 Hz and $J_{6a,6e}$ = 18 Hz
7, X = O_2CCH_3	1.99 (s)	1.50 1.50 1.42	5.34	4.88	1.75–1.55	1.86	2.2–1.95	2.44	0.76	see *a*

[a] $J_{4,5a} \simeq J_{5a,5e} \simeq J_{5a,6a} \simeq 12$ Hz, $J_{4,5e} \simeq J_{5a,6e} \simeq 6$ Hz, $J_{4,6e} \simeq 2$ Hz, $J_{5e} < 0.5$ Hz, $J_{6a,6e} \simeq 17$ Hz, $J_{3,4} \simeq 0.5$ Hz, and $J_{2,3} = 6.5$ Hz.

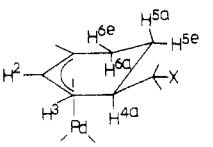


Figure 1.

A more systematic study of the oxypalladation of 1 was carried out in methanol. Treatment of 1 with $PdCl_2(MeCN)_2$ in methanol resulted in methoxypalladation of the cyclopropane ring to selectively give 5. Complexes 5 and 2 were formed in a ratio of 6:1 and in a total yield of 80%. It is interesting to note that no seven-membered ring product (i.e., 3 or its methoxy analogue) could be detected. When a more hindered alcohol such as cyclohexanol was used, the alkoxypalladation adduct 6 and 2 were formed in a ratio of 1.5:1 and the total yield dropped to 21%.

Analogous treatment of 1 with $PdCl_2(MeCN)_2$ in acetic acid resulted in a poor yield of the desired acetoxypalladation adduct 7. Complexes 7, 3, and 2 were formed in a ratio of 34:23:43 in a crude yield of 40–50%. Addition of 1 equiv of $LiOAc{\cdot}2H_2O$ depressed the formation of 3, and now 7 and 2 were formed in a ratio of 54:46 contaminated with 13% of unidentified material. The crude yield was 89%.

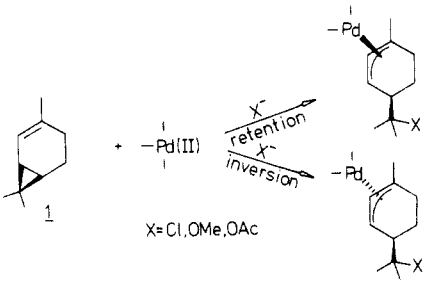
With use of column chromatography (flash chromatography) complexes 2, 3, 5, and 7 could be obtained pure for preparative purposes. The yield of isolated products after column chromatography, together with optical rotations and melting points are summarized in Table II.

Stereochemistry and Mechanism. The reaction rate of the chloropalladation of (+)-2-carene (1) in deuteriochloroform was measured by ^{1}H NMR. The reaction was found to obey second-order kinetics (eq 3), and the rate constant, k, was determined to 6×10^{-3} mol s^{-1}. No change in the reaction rate was observed on addition of cupric chloride, lithium chloride, or ethanol.

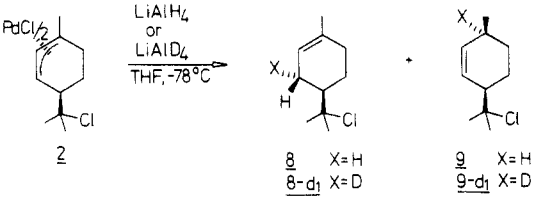
$$\text{rate} = k[\text{2-carene}][PdCl_2(MeCN)_2] \qquad (3)$$

An important question concerning the mechanism for the formation of 2, 3, 5, and 7 is whether the palladium(II)-induced ring opening takes place with retention or inversion of configuration at the carbon attacked by the metal. This is exemplified for the cleavage of the 1–7 bond leading to the six-membered ring complex, e.g., complexes 2, 5, and 7 (Scheme II). The complexes 2, 5, and 7 show very similar ^{1}H NMR spectra, indicating that they have the same configuration (Table III). Their spectra are consistent with the configuration shown in Figure 1. They all show a chemical shift separation between H^{5a} and H^{5e} of 1–1.7 ppm, with the H^{5a} proton at high field. Furthermore, the coupling constants $J_{4,5a} \simeq J_{5a,6a} \simeq J_{5a,5e} \simeq 12$ Hz in all three cases (Table III) require that the protons H^4, H^{5a}, and H^{6a} be pseudoaxial.

Scheme II



To obtain more conclusive evidence for the trans configuration of the palladium and the isopropyl group indicated by the ^{1}H NMR data, compound 2 was stereospecifically transformed to 8-d_1 and 9 (eq 4). Treatment



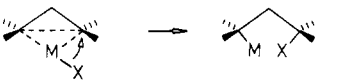
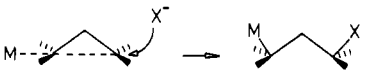
(4)

of 2 with $LiAlH_4$ afforded a mixture of 8 and 9 in a ratio of 4:1. From the ^{1}H NMR spectrum of 9 it follows that the methyl group and the isopropyl group are cis to one another (see Experimental Section). When 2 was reduced by $LiAlD_4$, 8-d_1 and 9-d_1 were formed in the same ratio (4:1). Importantly, the deuterium in 8-d_1 was found to be trans to the chloroisopropyl group (see Experimental Section). Since it is known[10] that $LiAlH_4$ cleaves (π-allyl)palladium bonds with retention of configuration at carbon, the results from the above mentioned reductions require that the palladium and the chloroisopropyl group in 2 are trans to one another. This shows that the ring opening of the cyclopropane giving the six-membered ring 2 has occurred with inversion of the configuration at carbon.

The configuration of the seven-membered ring π-allyl complex 3 is not readily determined from its ^{1}H NMR spectrum nor from chemical transformations. To determined whether the chloro group and palladium are cis or

(10) (a) Jones, D. N.; Knox, S. D. *J. Chem. Soc., Chem. Commun.* **1975**, 165. (b) Bäckvall, J. E.; Nordberg, R. E.; Björkman, E. E.; Moberg, C. *Ibid.* **1980**, 943. (c) Keinan, E.; Greenspoon, N. *Tetrahedron Lett.* **1982**, *23*, 241.

Table IV. Stereochemical Pathways[a] in Metal-Induced Nucleophilic Addition to Cyclopropanes

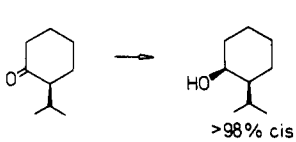
path	cyclopropane + M-X	stereochem at C-M	stereochem at C-X	overall stereochem of addition
1		ret	inv	trans
2		ret	ret	cis
3		inv	inv	cis
4		inv	ret	trans

[a] ret = retention; inv = inversion.

trans to one another, an X-ray crystal structure determination was made. The X-ray crystal of **3**, which has been published in detail elsewhere,[7b,11] unambigously established the configuration depicted in the drawing. Thus, the chloropalladation of **1** to give **3** has occurred trans.

Organic Transformations of 1 via 2, 5, and 7. One of the goals with the present study has been to establish transition-metal-catalyzed routes for organic transformations of (+)-2-carene. We have therefore studied some stoichiometric transformations of the π-allyl complexes **2**, **5**, and **7** shown in Scheme III. One reaction of great importance for a possible palladium-catalyzed oxidation of (+)-2-carene is the nucleophilic addition to the π-allyl group. Unfortunately attempted acetate attack on **2** using the conditions previously developed by us[10b,12] failed and led predominantly to elimination products. Reaction of **5** with sodium diethyl malonate in the presence of 1,2-bis(diphenylphosphino)ethane (diphos) afforded **10** as the only product. None of the other possible regioisomers could be detected.

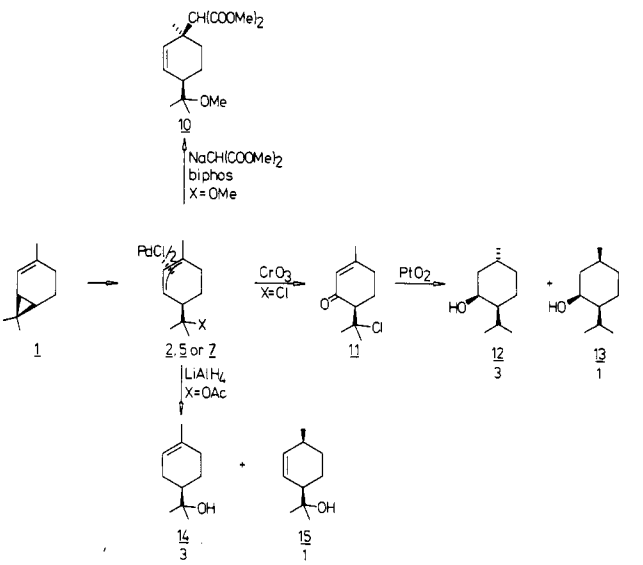
Oxidation of **2** by $Na_2Cr_2O_7$, using a procedure described by Jackson,[13] afforded the ketone **11** in moderate yield (25%). Subsequent hydrogenation in acetic acid using Adams catalyst produced neomenthol (**12**) and neoisomenthol (**13**) in a 3:1 ratio. Somewhat unexpectedly, the chloro–carbon bond was hydrogenated under the reaction condition. The high stereoselectivity for the hydroxy and isopropyl groups to become cis to one another is in accordance with the high cis selectivity in the reduction of 2-isopropylcyclohexanone to *cis*-2-isopropylcyclohexanol (eq 5).[14]



(5)

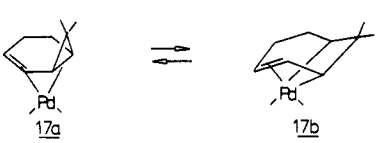
Reduction of complex **7** with $LiAlH_4$ gave a quantitative yield of α-terpineol (**14**) and its isomer **15** in a ratio of 3:1. The specific rotation of the purified α-terpineol is consistent with the one reported in the literature.[15]

Scheme III



Discussion

A mechanism that accounts for the stereochemical results is shown in Scheme IV. Thus, formation of a π-olefin complex, **16**, is expected to take place on the exo face of **1**. Now, cleavage of the 1–7 bond by palladium, giving the six-membered ring (π-allyl)palladium complex, must take place with inversion. Electrophilic activation of the 1–7 bond would develop a positive charge on C-7, which could be attacked by the nucleophile. On the other hand, the cleavage of the 1–6 bond, which leads to **3**, occurs with retention of configuration at the carbon that becomes attached to palladium. Coordination of the 1–6 bond of the cyclopropane gives a complex that has similarities with a η^4-1,3-diene complex. The other way of describing **17** is through a metallacyclobutane. The two extremes **17a** and **17b** are shown in eq 6. Nucleophilic attack by

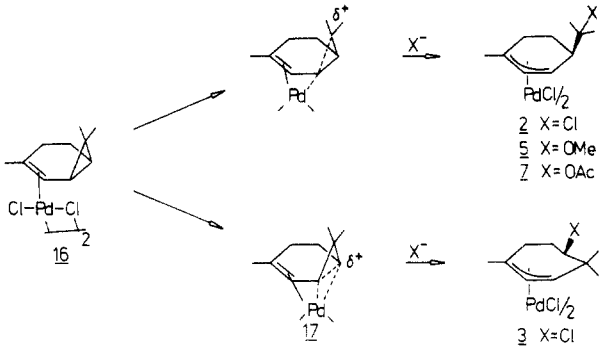


(6)

chloride with inversion of configuration accounts for the overall trans chloropalladation. It has been suggested[6b] that the initial step in the Pd(II)-induced opening of the cyclopropane ring in a vinylcyclopropane involves a cy-

(11) Björkman, E. E.; Bäckvall, J. E. *Acta Chem. Scand., Ser. A* **1983**, *A37*, 503.
(12) Bäckvall, J. E.; Nordberg, R. E. *J. Am. Chem. Soc.* **1981**, *103*, 4959.
(13) Gray, G. A.; Jackson, W. R.; Rooney, J. J. *J. Chem. Soc. C* **1970**, 1788.
(14) Hückel, W.; Neidlein, R. *Chem. Ber.* **1958**, *91*, 1391.
(15) Hückel, W.; Wolowski, H. *Chem. Ber.* **1947**, *80*, 39.

Scheme IV



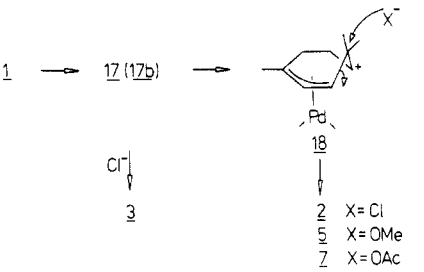
clopropylcarbinyl cation intermediate, formed by donation of an electron pair from the olefin to the palladium.

In principle there are four sterically different pathways of adding a metal and a nucleophile to a cyclopropane (Table IV). Of these pathways the one with inversion at the carbon center forming the C–M bond and retention at the carbon center forming the C–X bond can be excluded since it implies a nucleophilic substitution with retention (path 4). In this work, additions according to path 1 (1 → **3**) and path 3 (1 → **2**) have been shown to take place.

The ring opening of a specifically deuterated cyclopropane with platinum(II) to give a metallacyclobutane has been shown to take place with retention at both carbon atoms (cf. path 1 and 2).[4] Furthermore, it has been reported that chloropalladation of an allylic cyclopropane (bicyclo[5.1.0]oct-3-ene) occurs with trans stereochemistry[5b] but that chloropalladation of a homoallylic cyclopropane (bicyclo[5.1.0]oct-4-ene takes place with cis stereochemistry.[5a] The former is explained by path 1 (ret, inv), but the latter was originally interpreted as an addition involving coordinated chloride giving retention at both carbon centers (cf. path 2). More recently, however, examples have been reported where an overall cis addition is the result of inversion at both carbon centers (cf. path 3).[5d,7a] This is in accordance with the observed inversion at both carbons in the oxymercuration of cyclopropanes.[9a] There are so far no examples reported where a chloride ligand migrates from palladium to a coordinated cyclopropane or coordinated alkene. On the other hand external attack by chloride (with inversion) on coordinated cyclopropanes (cf. path 1)[5b,7b] and coordinated alkenes[16] has been shown in several instances. As pointed out previously, chloride attack at a carbon atom bound to palladium with inversion is a much more favored process than the corresponding migration to carbon with retention.[7b,17]

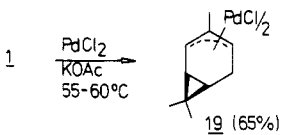
The mechanism of the corresponding chloropalladation of a methylenecyclopropane has recently been investigated.[8] 1,3-Chloropalladation of *cis*- and *trans*-9-methylenebicyclo[6.1.0]nonane was shown to take place with overall cis stereochemistry (ret, ret or inv, inv), whereas chloropalladation of *cis*-7-methylenebicyclo-[4.1.0]heptane was shown to occur with overall trans stereochemistry (ret, inv).[8b] The authors proposed that the latter case is a result of an isomerization of a kinetically cis 1,3-chloropalladation product, and they favored a concerted mechanism for the cis chloropalladation.

Scheme V



Another possible pathway for the formation of **2**, **5**, and **7** from **1**, involving a rearrangement, must also be considered (Scheme V). This path proceeds via formation of the intermediate **18** from **17** followed by rearrangement and nucleophilic attack. We cannot distinguish between the mechanisms in Schemes IV and V with the present data. A similar rearrangement of an iridacyclobutane has been reported by Jennings.[18] We also conclude that such a rearrangement must be considered also in oxymercurations and other electrophilic cleavages of cyclopropanes that occur with inversion at the carbon attacked by the electrophile.[9b]

The drastic change in product selectivity with reaction conditions for the reaction of **1** with palladium(II) is remarkable. Increasing the polarity of the solvent is expected to increase the electrophilicity at the tertiary center of **1**. The nucleophilic attack at the tertiary center may change to an SN1-type reaction on going to a more polar solvent. The same argument also holds for the mechanism in Scheme V. In the latter case the driving force would be the formation of a more stable carbonium ion. The solvent effect therefore does not distinguish between the two mechanisms. It is interesting to note that reaction of (+)-2-carene (**1**) with palladium chloride in acetic acid in the presence of potassium acetate has recently been reported[19] to give (π-allyl)palladium complex **19**.



Conclusions

The ring opening of vinylcyclopropanes by palladium(II) and a nucleophile may take place with different stereochemistry depending on the reaction conditions. For chloropalladation of **1** → **3** (in benzene) the metal–carbon bond formation takes place with retention of configuration at carbon, whereas for chloropalladation of **1** → **2** (in chloroform–ethanol) the metal–carbon bond formation takes place with inversion. In a nucleophilic solvent such as methanol or acetic acid an oxypalladation of **1** takes place. The mechanism of the oxypalladation is similar to the one of the chloropalladation of **1** → **2**, i.e., with inversion at the carbon center forming the metal–carbon bond.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 257 spectrophotometer. ^1H and ^{13}C NMR spectra were obtained with a Bruker WP 200 FT spectrometer at 200 and 50.3 MHz, respectively. Chemical shifts are reported in δ units (ppm) downfield from tetramethylsilane. GLC analyses were performed on a 2.4 m × 6 mm glass column packed with 5% SE-30 on Chromosorb

(16) (a) Wiger, G.; Albelo, G.; Rettig, M. F. *J. Chem. Soc., Dalton Trans.* **1974**, 2242. (b) Wipke, W. T.; Goeke, G. L. *J. Am. Chem. Soc.* **1974**, *96*, 4244.

(17) A recent theoretical treatment of cis migration of coordinated nucleophiles in (π-olefin)palladium complexes indicate that coordinated fluoride (and also chloride) will not readily migrate to the coordinated olefin: Bäckvall, J. E.; Björkman, E. E.; Pettersson, L. Sieghbahn, P. *J. Am. Chem. Soc.* **1984**, *106*, 4369.

(18) Campbell, W. H.; Jennings, P. W. *Organometallics* **1983**, *2*, 1460.

(19) Horiuchi, C. A.; Satoh, J. Y. *J. Organomet. Chem.* **1983**, *258*, C45.

W. High-pressure liquid chromatography (HPLC) was run on a Waters M-45 instrument with a μ-Porasil column (silica, 10 μm packing, 0.4 × 30 cm). Melting points are uncorrected.

Analytical grade ("pro-analysi") chloroform, benzene, and methanol were purchased from FLUKA AG and used without further purification. Tetrahydrofuran (THF) was distilled from a deep blue solution of potassium/benzophenone under nitrogen. (+)-2-Carene ((+)-3,7,7-trimethylbicyclo[4.1.0]hept-2-ene) was a gift from Dr. Günther Ohloff (Firmenich, Geneva) and Professor Sukh Dev (Malti-Chem Research Center, India). Palladium chloride was obtained from Engelhard and converted to $PdCl_2(CH_3CN)_2$ by stirring overnight in acetonitrile and collecting the resulting yellow crystals by filtration. In all preparative reactions between (+)-2-carene and Pd(II), small amounts of cupric chloride were added in order to avoid precipitation of Pd(0).

Reaction of (+)-2-Carene (1) with $PdCl_2(CH_3CN)_2$. Complex 2. To a stirred slurry of $PdCl_2(CH_3CN)_2$ (259 mg, 1 mmol) and $CuCl_2 \cdot 2H_2O$ (17 mg, 0.1 mmol) in chloroform (5 mL, analytical grade: contains 0.6–1% of ethanol) at ambient temperature under nitrogen was added absolute ethanol (70 μL) followed by (+)-2-carene (1) (180 μL, 150 mg, 1.1 mmol). The mixture was stirred at ambient temperature for 8 h, and then the solvent was removed on a rotary evaporator in vacuo. The brown residue was dissolved in 2 mL of CH_2Cl_2, filtered through a short column of alumina (neutral), and eluted with more CH_2Cl_2. Rotary evaporation of the solvent in vacuo afforded 281 mg (90%) of a yellow oil as a mixture of complexes **2**, **3**, and the ethoxy complex **4** (see Table I). The crude product was purified by flash column chromatography on silica. Elution with CCl_4/CH_2Cl_2 (3/2) gave first 43 mg (13%) of **3** followed by 194 mg (62%) of **2**. Finally elution with $CHCl_3$ afforded 35 mg (10%) of **4**. The complex **2** is pure from this procedure but may be recrystallized from CH_2Cl_2–hexane to obtain an analytical sample: IR (KBr) 3050, 2990–2900, 1450, 1430, 1390, 1375, 1115 cm^{-1}; ^1H NMR, see Table III; ^{13}C NMR ($CDCl_3$) δ 101.7, 95.8, 73.5, 71.7, 51.6, 34.6, 30.9, 30.3, 24.7, 21.1.

Anal. Calcd for $C_{20}H_{32}Cl_4Pd_2$: C, 38.31; H, 5.14. Found: C, 38.48; H, 5.17.

4: IR (CCl_4) 3030, 2990, 2900, 1445, 1430, 1390, 1370, 1150, 1070 cm^{-1}; ^1H NMR, see Table III.

Complex 3. $PdCl_2(CH_3CN)_2$ (1.04 g, 4 mmol), **1** (600 mg, 4.4 mmol), and $CuCl_2 \cdot 2H_2O$ (68 mg, 0.4 mmol) were stirred in benzene (20 mL) for 40 h. The same workup procedure as above using column chromatography (silica, CCl_4/CH_2Cl_2 = 3/2) afforded 640 mg (51%) of **3**: IR (KBr) 3030, 2990–2900, 1470, 1455, 1380, 1370 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.65 (d, J = 9 Hz, 1 H), 4.48 (br d, J = 9 Hz, 1 H, CHCl), 4.43 (d, 1 H, J = 9 Hz), 2.34 (m, 1 H), 2.12 (m, 1 H), 2.0–1.8 (m, 2 H), 1.51 (s, 3 H), 1.46 (s, 3 H), 1.18 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 100.2, 99.7, 85.5, 69.3, 44.1, 37.5, 31.5, 30.3, 28.3, 24.7.

Anal. Calcd for $C_{20}H_{32}Cl_4Pd_2$: C, 38.31; H, 5.14. Found: C, 38.55; H, 5.19.

Complex 5. The same procedure was used but the solvent was replaced by methanol. Reaction for 43 h followed by the same workup with column chromatography (silica, $CHCl_3$) afforded **5** in an isolated yield of 67%: IR (CCl_4) 3030, 2990–2900, 1440, 1430, 1385, 1370, 1150, 1080 cm^{-1}; ^1H NMR, see Table III; ^{13}C NMR ($CDCl_3$) δ 101.7, 94.9, 76.0, 75.1, 49.2, 46.7, 35.2, 24.8, 22.7, 22.6, 20.6.

Anal. Calcd for $C_{22}H_{38}Cl_2O_2Pd_2$: C, 42.74; H, 6.20. Found: C, 42.88; H, 6.21.

Complex 7. To a stirred slurry of $PdCl_2(CH_3CN)_2$ (259 mg, 1 mmol), $CuCl_2 \cdot 2H_2O$ (43 mg, 0.25 mmol), and $LiOAc \cdot 2H_2O$ (102 mg, 1 mmol) in acetic acid (5 mL) at ambient temperature under nitrogen was added **1** (180 μL, 150 mg, 1 mmol). The mixture was stirred at ambient temperature for 15 h, and then the acetic acid was removed in vacuo (1 mm) using a Kügelrohr apparatus. The residue was dissolved in CH_2Cl_2 and filtered through a short column of alumina (neutral). Rotary evaporation of the solvent in vacuo afforded 277 mg of a yellow oil. The crude product was purified by flash column chromatography on silica. Elution with CCl_4/CH_2Cl_2 = 3/2 gave first 34 mg of unidentified material and then 106 mg (34%) of complex **2**. Finally, elution with chloroform afforded 128 mg (38%) of the acetoxy complex **7**: IR (CCl_4) 3030, 2990–2900, 1740, 1450, 1435, 1390, 1375, 1260, 1225, 1130, 1020 cm^{-1}; ^1H NMR, see Table III; ^{13}C NMR ($CDCl_3$) δ 170.1, 101.4, 95.4, 82.7, 73.6, 48.7, 34.8, 24.8, 23.6, 22.8, 22.4, 20.4.

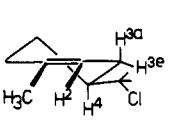
Anal. Calcd for $C_{24}H_{38}Cl_2O_4Pd_2$: C, 42.75; H, 5.68. Found: C, 42.78; H, 5.72.

Reduction of 2 with $LiAlH_4$. 8 and 9. To a cold (−78 °C) solution of **2** (115 mg, 0.18 mmol) in THF (2 mL) was added $LiAlH_4$ (28 mg, 0.73 mmol) under nitrogen. Ethene gas was bubbled through the solution in order to avoid hydrogenation of the double bond. Immediately a black precipitation of Pd(O) was observed. After the solution was stirred at −78 °C for 1 h, the solution was allowed to warm to −10 °C and ethyl acetate (2 mL) and 2 M NaOH (2 mL) were added. After the solution was stirred at ambient temperature for a few minutes, ether (3 mL) was added and the mixture was filtered through a glass filter. The solid was washed with ether (4 × 1.5 mL) and 2 M NaOH (2 mL). The water phase was extracted with ether (2 × 3 mL), and the combined organic phases were washed with 2 M NaOH (3 mL) and brine (3 mL) and dried ($MgSO_4$). The solvent was removed in vacuo to afford 61 mg (96%) of a light yellow liquid, consisting of **8** and **9** in a ratio of 4:1 (determined by ^1H NMR and GLC). The two isomers were separated by preparative GLC [5% SE-30 on Chromosorb W, 120 °C, **8** (8,3 min) and **9** (7.2 min)].

8:[20] ^1H NMR ($CDCl_3$) δ 5.37 (m, W_H = 10.4 Hz, 1 H, C=CH), 2.16 (br d, J = 16 Hz, 1 H, C=CHCH^e), 2.09–1.7 (m, 6 H, $CH_2CH_2CHCH^a$), 1.66 (br s, 3 H, CH_3C=C), 1.59 (s, 3 H, CH_3CCl), 1.55 (s, 3 H, CH_3CCl).

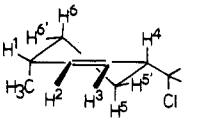
9: ^1H NMR ($CDCl_3$) δ 5.77 (s, 2 H, HC=CH), 2.41 (8 m, 1 H, CHCCl), 2.21 (m, 1 H, CHCH_3), 1.8–1.4 (m, 4 H, CH_2CH_2), 1.60 (s, 3 H, CH_3CCl), 1.53 (s, 3 H, CH_3CCl), 0.99 (d, J = 7.3 Hz, 3 H, CH_3CH).

Detailed analysis of the ^1H NMR spectra ($CDCl_3$) including decoupling experiments led to the following coupling constants:



8

$J_{3e,3a}$ = 16 Hz
$J_{3e,2}$ = 4.4 Hz
$J_{3e,4}$ < 5 Hz



9

$J_{1,6}$ or $J_{1,6'}$ = 5.4 Hz, $J_{4,5}$ = 9.3 Hz
$J_{1,6}$ or $J_{1,6'}$ = 2.7 Hz, $J_{4,5'}$ = 4.5 Hz
$J_{1,4}$ = 2.2 Hz, $J_{3,4}$ = 0.5 Hz
$J_{1,2}$ = 1–1.4 Hz

Reduction of 2 with $LiAlD_4$. 8-d_1 and 9-d_1. A mixture of 8-d_1 and 9-d_1 was prepared by using the same procedure as above. The palladium complex **2** (89 mg, 0.28 mmol), $LiAlD_4$ (23 mg, 0.56 mmol), and THF (1.5 mL) afforded after workup 46 mg (94%) of a light yellow liquid.

8-d_1: ^1H NMR ($CDCl_3$) as for **8** but H^2 at δ 5.37 showed W_H = 6.0 Hz and H^{3e} at 2.16 ppm was absent.

9-d_1: ^1H NMR ($CDCl_3$) as for **9** but H^1 at δ 2.21 ppm was absent.

Configurational Assignment of 8-d_1 and 9. The proton at δ 2.16 of **8** was assigned as H^{3e} since $J_{3e,4}$ < 5 Hz. The absence of H^{3e} in 8-d_1 shows that deuterium and the isopropyl group are trans to one another.

The coupling constants of **9**, $J_{1,6}$ and $J_{1,6'}$, being <5.5 Hz, together with the fact that $J_{4,5}$ = 9.3 Hz, are consistent only with the methyl and isopropyl groups being cis to one another in the conformation shown for **9**.

Reaction of 5 with $NaCH(COOMe)_2$. Compound 10. To a suspension of sodium hydride (48 mg, 2 mmol) in anhydrous THF (15 mL) under nitrogen was added dimethyl malonate (277 mg, 2.1 mmol). The solution was stirred for 15 min. In another flask 1,2-bis(diphenylphosphino)ethane (398 mg, 1 mmol) and complex **5** (309 mg, 0.5 mmol) in 15 mL of anhydrous THF were stirred under nitrogen for 15 min. To this solution was added the first solution of sodium dimethyl malonate, and the reaction mixture was stirred at ambient temperature for 18 h. Water was added, and the solution was extracted with ether. The combined organic layers were washed with water and dried ($MgSO_4$). The solvent was evaporated in vacuo, and the low boiling components (dimethyl malonate and elimination product) were removed on a Kughelrohr distillation apparatus. The remaining crude product was purified by flash column chromatography (silica, hexane/ethyl

(20) Carman, R. M.; Shaw, I. M. *Aust. J. Chem.* **1976**, *29*, 133.

acetate = 70/30) to afford 220 mg (74%) of **10**: IR (CCl_4) 3030, 3000–2900, 1765, 1740, 1460, 1440, 1330, 1235, 1200, 1150, 1080, 1030 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.71 (m, 2 H, CH=CH), 3.72 (s, 3 H, OMe), 3.70 (s, 3 H, OMe), 3.51 (s, 1 H, *CH*(COOMe)$_2$), 3.20 (s, 3 H, OMe), 2.36–2.24 (m, 1 H), 2.1–1.97 (m, 1 H), 1.75–1.27 (m, 3 H), 1.24 (s, 3 H, CH_3), 1.12 (s, 3 H, CH_3), 1.10 (s, 3 H, CH_3).

Anal. Calcd for $C_{16}H_{26}O_5$: C, 64.41; H, 8.78. Found: C, 63.88; H, 8.59.

Oxidation of 2 to 11. To a solution of 983 mg (3.3 mmol) of $Na_2Cr_2O_7 \cdot 2H_2O$ in sulfuric acid (0.7 mL)–water (3.6 mL)–ether (10 mL) was added 563 mg (0.9 mmol) of complex **2**. The mixture was stirred at ambient temperature for 2 h and then extracted with ether. The combined organic layers were washed with water and dried ($MgSO_4$). The solvent was removed on a rotary evaporator in vacuo, and the residue was purified by flash column chromatography (silica, pentane/ether = 80/20) affording 83 mg (25%) of **11** as a colorless liquid: $[\alpha]^{20}_D$ +39.6° ($CHCl_3$); IR (CCl_4) 3040, 2980, 2940, 2880, 1675, 1645, 1545, 1385, 1370, 1210, 1110 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.80 (br s, 1 H, CH=C), 2.58 (m, 2 H), 2.45–2.35 (m, 2 H), 2.01 (m, 1 H), 1.94 (br s, 3 H, CH_3C=C), 1.91 (s, 3 H, CH_3), 1.66 (s, 3 H, CH_3).

Catalytic Hydrogenation of 11. Neomenthol (12) and Neoisomenthol (13). Ketone **11** (70 mg, 0.37 mmol) and Platinum black[21] (7 mg, 0.036 mmol) were stirred in acetic acid (0.7 mL) under an atmospheric pressure of hydrogen at ambient temperature for 8 h. The reaction mixture was filtered, and the precipitate was washed with ether (5 mL). Water (2 mL) and saturated NaCl solution (2 mL) were added, and the mixture was stirred in a separatory funnel. After collection of the organic layer the aqueous phase was further extracted with ether (2 × 5 mL). The combined organic layers were washed with water (2 mL) and 2 M $NaHCO_3$ (2 × 2 mL) and dried ($MgSO_4$). Rotary evaporation of the solvent in vacuo afforded 54 mg (92%) of menthol isomers. According to ^1H NMR the main components (>90%) were neomenthol (**12**)[22] and neoisomenthol (**13**)[23] in a ratio of 3:1. Small amounts of menthol[24] (5–10%) could be detected in the ^1H NMR spectrum. Distinguishable signals in the ^1H NMR ($CDCl_3$): neomenthol, δ 4.12 (CHO); neoisomenthol, δ 4.03 (CHO); menthol, δ 3.45 (CHO).

Reduction of 7 with $LiAlH_4$. α-Terpineol (14) and 15. To a solution of **7** (100 mg, 0.15 mmol) in anhydrous THF (2 mL) under nitrogen at −78 °C was added 27 mg (0.7 mmol) of $LiAlH_4$. Ethene was bubbled through the solution, which was stirred for 2 h at −78 °C and then for 1 h at −30 °C. The mixture was allowed to slowly warm up to 0 °C (1–2 h) and then quenched with water and 2 M NaOH. The precipitate was removed by filtration and washed several times with ether. The organic phase of the filtrate was collected, and the aqueous phase was extracted with ether. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo on a rotary evaporator to afford 45 mg (98%) of a 3:1 mixture of **14** and **15** according to ^1H NMR. The products were separated and purified by HPLC (hexane/ethyl acetate = 90/10). The main product was shown to be **14**, whose ^1H NMR spectrum and specific rotation are consistent with that of an authentic sample of (+)-α-terpineol: $[\alpha]^{20}_D$ +96.9° (EtOH) (lit.[15] $[\alpha]^{20}_D$ +98.4° (EtOH)).

15:[25] ^1H NMR ($CDCl_3$) δ 5.85–5.65 (m, 2 H, CH=CH), 2.3–2.05 (m, 2 H, allylic CH), 1.8–1.35 (m, 4 H, CH_2CH_2), 1.30 (br s, 1 H, OH), 1.21 (s, 3 H, CH_3), 1.17 (s, 3 H, CH_3), 0.98 (d, 3 H, CH_3).

Acknowledgment. We are grateful to the "Jacob Wallenberg Foundation", "Tryggers Stiftelse", and the Swedish Natural Science Research Council for financial support. We are indebted to Drs. Sukh Dev and Günther Ohloff for samples of (+)-2-carene.

Registry No. **1**, 4497-92-1; **2**, 82740-38-3; **3**, 82740-39-4; **4**, 96395-36-7; **5**, 96411-95-9; **6**, 96411-96-0; **7**, 96411-97-1; **8**, 58865-12-6; **8**-d_1, 96395-37-8; **9**, 82795-79-7; **9**-d_1, 96395-38-9; **10**, 96395-39-0; **11**, 96395-40-3; **12**, 2216-52-6; **13**, 64282-88-8; **14**, 7785-53-7; **15**, 23727-04-0.

(21) Prepared according to Feulgen, R. *Chem. Ber.* **1921**, *54*, 360.
(22) Eliel, E. L.; Gianni, M. H.; Williams, Th. H.; Stothers, J. B. *Tetrahedron Lett.* **1962**, 741.
(23) Feltkamp, H.; Franklin, W. C. *Tetrahedron* **1965**, *21*, 1541.
(24) Varian Catalog Vol. 1, Spec. No. 281, 1962.
(25) Schwartz, M. A.; Swanson, G. C. *J. Org. Chem.* **1979**, *44*, 953.

A Kinetic Study of the 1,2-Hydrogen Shift in a Bis(η-cyclopentadienyl)tungsten System

Jennifer C. Green,* Malcolm L. H. Green, and Christopher P. Morley

Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, England

Received August 13, 1984

The rate of the thermal isomerization of $[W(\eta\text{-}C_5H_5)_2(H)(CH_2PMe_2Ph)]^+$ (A) to $[W(\eta\text{-}C_5H_5)_2(CH_3)(PMe_2Ph)]^+$ (B) in acetone solution with hexafluorophosphate as counterion has been measured under a variety of conditions. The rate is found to be first order in *A* ($k_{70°C}$ = (3.2 ± 0.08) × 10^{-6} s^{-1}), strongly temperature dependent (E_A = 144.7 ± 3.6 kJ mol^{-1}), essentially independent of free phosphine concentration, and enhanced by deuteration of the "active" methyl group (k_H/k_D(70 °C) = 0.80 ± 0.02). Hydrogen migration is involved in the rate-determining transition state of the reaction, and simple reversible phosphine dissociation to a cationic metal carbene intermediate is too simple a mechanism to account for all the results. Two alternative mechanisms are proposed, one involves the formation of an agostic methyl intermediate, $[W(\eta\text{-}C_5H_5)_2(CH_2)(\mu\text{-}H)]^+$, and the other an equilibrium between a carbene hydride, $[W(\eta\text{-}C_5H_5)_2(CH_2)(H)]^+$, and a methyl cation, $[W(\eta\text{-}C_5H_5)_2(CH_3)]^+$.

Introduction

The 1,2-hydrogen shift (α-elimination) has lately become recognized as an important mechanistic possibility in organo-transition-metal chemistry and in at least one case[1] has been observed directly. Recent work by several authors, reviewed by Brookhart and Green,[2] has demonstrated that such a hydrogen transfer from ligand to metal in transition-metal hydrocarbyl complexes may often

(1) Turner, H. W.; Schrock, R. R.; Fellman, J. D.; Holmes, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 4942.
(2) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

0276-7333/85/2304-1302$01.50/0