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CIS-OXYPALLADATION COMPLEXES OF A PINENE DERIVATIVE

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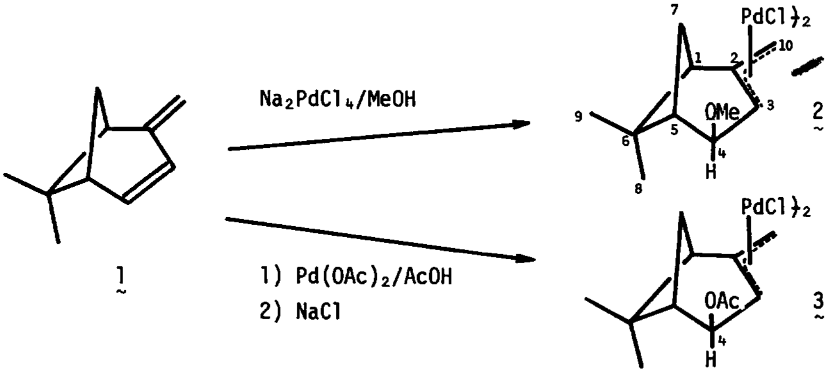
Abstract. 4-Methoxy- and 4-acetoxy(3,2,10-η-pinene)palladium complexes prepared from dehydro-β-pinene with Na_2PdCl_4 in MeOH and $Pd(OAc)_2$ in AcOH, respectively, represent the first isolated *cis*-oxypalladation adducts.

Palladium(II)-induced nucleophilic addition to olefins has been extensively studied from both synthetic and mechanistic aspects.[1] In particular, the stereochemical mode of the addition has attracted much attention. It appears to be one of general agreements that oxygen nucleophiles such as acetate, alcohol, and water attack on π-olefin and σ-alkylpalladium complexes in a *trans*-fashion.[2] Recently, a new observation on this regard has been put forward in which acetate can add *cis* for π-allylpalladium complexes.[3] This result prompts us to report our own work on the first isolation of *cis*-oxypalladation complexes derived from the attack of alcohol and acetate on a pinene derivative co-ordinated to palladium.

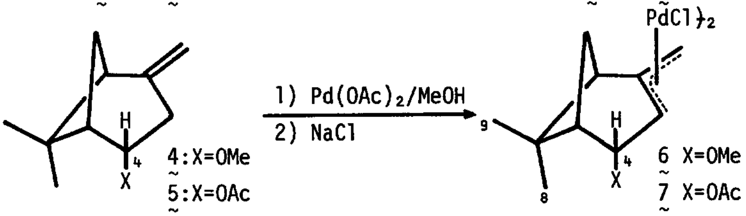
During the course of our investigation on the Pd(II)-catalyzed asymmetric cyclization of 2-allylphenols,[4] we have prepared a variety of η^3-pinenepalladium complexes. When dehydro-β-pinene (1) was allowed to react with an equimolar amount of Na_2PdCl_4 in MeOH at room temperature for 1 hr, the π-allyl complex 2 was obtained as a single product in 53% isolated yield.[5] Treatment of 1 with $Pd(OAc)_2$ in AcOH followed by addition of NaCl gave the complex 3 in 47% yield. The reaction of 1 with $Pd(OAc)_2$ in MeOH under the same conditions resulted in the formation of both complexes 2 and 3 in 12 and 14% yields, respectively.

The following results allow us to assign that 2 and 3 are the *cis*-oxypalladation complexes as depicted in eq. 1. (i) π-Allylpalladium complexes 6 and 7, which have the *trans*-configuration



(eq. 1)

between Pd and the C-4 substituents (OMe and OAc), were independently prepared from the β-pinenes 4 and 5 of known stereochemistry,$^{6)}$ as shown in eq. 2. Thus, the complex 6 was obtained in 52% yield from the compound 4 bearing the C-4 substituent (X=OMe) at the same site of the *gem*-dimethyl group, upon treatment with $Pd(OAc)_2$ in MeOH followed by addition of NaCl. Similarly, 7 was obtained from 5 (X=OAc) in 58% yield. Comparison of the spectral data in the Table shows that the complexes 2 and 3 are different from corresponding 6 and 7. (ii) When the relative chemical shifts for the *gem*-dimethyl group (Δδ 8-Me and 9-Me) of 2, 3, 6, and 7 were compared with those of the corresponding parent α-pinenes, any meaningful shift could not be detected. If the palladium in the complexes is in the same site of the *gem*-dimethyl group, the relative chemical shift must be greatly affected by the proximity between the metal and one of the methyl groups.$^{7)}$ Therefore, the configuration between Pd and the C-4 substituent is determined to be *trans* for 6 and 7 and *cis* for 2 and 3.$^{8)}$



(eq. 2)

Table. Representative NMR Shifts of π-Allyl Complexes (100 MHz, $CDCl_3$, δ)

Complex	8-Me	9-Me	H-10		H-3	H-4	$J_{3,4}$(Hz)	$J_{4,5}$(Hz)
2	0.99	1.39	3.03	3.73	3.99	3.52	4.5	2.5
3	1.04	1.40	3.08	3.69	4.15	4.88	5.0	2.6
6	1.11	1.38	3.08	3.75	3.96	3.65	0	2.4
7	1.13	1.39	3.09	3.77	3.89	3.65	0	2.4

References and Notes

1) For a comprehensive review , see P. M. Henry "Palladium Catalyzed Oxidation of Hydrocarbon", D. Reidel: Holland, 1980; pp 44-223.

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5) Satisfactory elemental analyses for all the complexes reported herein were obtained. Yields are based on isolated products by preparative TLC (SiO_2, EtOAc n-hexane=1:4).

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8) The complexes 2 and 3 are the primary products in the present reactions, since 6 and 7 are not converted into 2 and 3 under the reaction conditions, respectively.

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