least in the latter case). Thus our results to date highlight the great need for kinetic experiments on fixed-site systems (at constant $\Delta E^\circ$) in which systematic variations in through-space and through-bond distances can be investigated thoroughly.

**Acknowledgment.** We thank Stephen Mayo for invaluable assistance.[6e] Helpful comments were provided by David Blair, Jonathan Caspar, Walther Ellis, Karl Freed, Michel Goldberg, Brian Hoffman, John Hopfield, Noel Hush, Sven Larsson, George McLendon, Bo Malmström, Rudy Marcus, and Israel Pecht. This research was supported by National Institutes of Health Grant AM19038.

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# Stereochemistry of Oxidative Addition of an Optically Active Allyl Acetate to a Palladium(0) Complex

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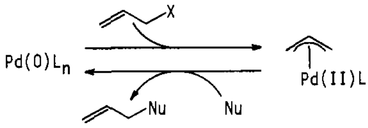
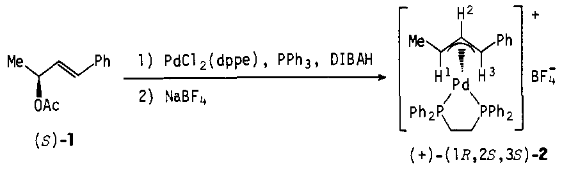
*Received July 27, 1983*

There has been considerable synthetic and mechanistic interest in palladium-catalyzed allylation of nucleophiles with allylic compounds represented by allyl acetates.[1] The catalytic cycle of the allylation is generally accepted to involve a $\pi$-allylpalladium(II) complex as a key intermediate, which is formed by oxidative addition of an allyl acetate to palladium(0) and undergoes nucleophilic attack to yield allylation product and to regenerate palladium(0)[1] (Scheme I). The nucleophilic attack has been reported to proceed with either inversion[2-6] or retention[7-9] of configuration depending on the nature of nucleophiles, and the stereochemistry of the oxidative addition has been deduced[3,10] to be inversion by stereochemical results obtained for the catalytic allylation[3,10-19] and stoichiometric reaction of $\pi$-allylpalladium complexes with nucleophiles.[2-9] However, there has been no direct evidence to support the stereochemistry of the oxidative addition. Here we report the isolation of an optically active $\pi$-allylpalladium complex from a mixture of an optically active allyl acetate and a palladium(0) complex,[20] which unambiguously demonstrates, for the first time, that the oxidative addition forming $\pi$-allylpalladium(II) proceeds with inversion of configuration.[21]

Scheme I

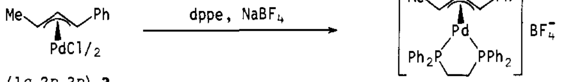


An excess of (*S*)-(*E*)-3-acetoxy-1-phenyl-1-butene (**1**) (58% ee)[22] was added to an ethereal solution containing a palladium(0) complex, presumably Pd(dppe)(PPh$_3$) (dppe = 1,2-bis(diphenylphosphino)ethane),[23] generated in situ by treatment of a mixture of PdCl$_2$(dppe) and 1 equiv of triphenylphosphine with 2 equiv of diisobutylaluminum hydride (DIBAH). The mixture was stirred at room temperature for 12 h, and sodium tetrafluoroborate was added (eq 1). Aqueous workup (extraction with chloroform) followed by preparative TLC on silica gel (hexane/EtOAc (1/4), $R_f$ 0.1–0.2) gave 44% yield[25] of cationic $\pi$-allylpalladium complex **2** with optical rotation of $[\alpha]^{20}_D$ +57° (*c* 0.8, chloroform). **2**: Anal. Calcd for $C_{36}H_{35}P_2BF_4Pd$: C, 59.82; H, 4.88; P, 8.57. Found: C, 59.88; H, 4.82; P, 8.55. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 1.66 (dt, 3 H, Me), 2.28–2.72 (m, 4 H, PCH$_2$CH$_2$P), 4.42 (ddq, 1 H, H$^1$), 5.11 (dd, 1 H, H$^3$), 6.16 (t, 1 H, H$^2$), 6.76–7.73 (m, 25 H, Ph); $J(H^1-H^2) = J(H^2-H^3) = 12.8$, $J(H^1-Me) = 6.3$, $J(H^1-P) = 9.5$, $J(H^3-P) = 10.8$, $J(Me-P) = 9.4$ Hz. The NMR shows that both methyl and phenyl substituents in the $\pi$-allyl system are located in the syn positions with respect to the central hydrogen, and both the diphenylphosphino groups in the dppe coordinate to the palladium to form a chelate.



(*S*)-**1** (+)-(1*R*,2*S*,3*S*)-**2** (1)

The absolute stereochemistry and enantiomeric purity of **2** obtained above were conveniently determined by comparison of its optical rotation with that of an authentic sample prepared through a different pathway (eq 2). Thus, (1*S*,2*R*,3*R*)-di-$\mu$-chlorobis(1-methyl-3-phenyl-$\pi$-allyl)dipalladium (**3**)[26] (86% ee, $[\alpha]^{20}_D$ −604° (*c* 1.0, chloroform)) was treated with dppe and sodium tetrafluoroborate in chloroform[2] to give quantitatively the palladium complex **2** with $[\alpha]^{20}_D$ −105° (*c* 1.1, chloroform), which must have the same configuration and enantiomeric purity as those of the starting **3**. It follows that the $\pi$-allylpalladium **2** obtained



(1*S*,2*R*,3*R*)-**3** (−)-(1*S*,2*R*,3*R*)-**2** (2)

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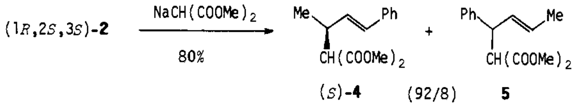
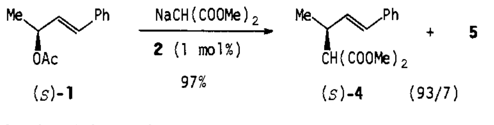
from the acetate (*S*)-**1** is a 1*R*,2*S*,3*S* isomer of 47% ee, indicating that the oxidative addition proceeded with inversion in 81% stereoselectivity.[27]

The $\pi$-allylpalladium 1,2-bis(diphenylphosphino)ethane complex (1*R*,2*S*,3*S*)-**2** (47% ee) was allowed to react with dimethyl sodiomalonate in THF to give 74% yield of (*S*)-dimethyl[1-((*E*)-styryl)ethyl]malonate[28] (**4**) ($[\alpha]^{20}_{D}$ −26° (*c* 0.8, chloroform), 38% ee) and 6% yield of its regioisomer **5** (eq 3). Use of the complex **2** as a catalyst (1 mol %) for the reaction of (*S*)-**1** (58% ee) with dimethyl sodiomalonate brought about the formation of (*S*)-**4**[28] ($[\alpha]^{20}_{D}$ −40° (*c* 1.0, chloroform), 58% ee) in a high yield (eq 4). These stereochemical results, inversion and retention obtained here for the stoichiometric and catalytic alkylation, respectively, confirm those reported by use of diasteromeric $\pi$-allylpalladium complexes[2–4] and allylic acetates.[10–13]



(3)



(4)

Thus, the stereochemistry in each step of the catalytic cycle has been verified in the enantiomeric system: inversion at the oxidative addition and inversion at the alkylation of $\pi$-allylpalladium with dimethyl sodiomalonate, leading to net retention in catalytic alkylation.

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[27] The loss of enantiomeric purity may be attributable to attack of acetate anion on the $\pi$-allyl moiety from the same side as palladium, which generates (*R*)-**1**. See ref 10 and: Bäckvall, J.-E.; Nordberg, R. E. *J. Am. Chem. Soc.* **1981**, *103*, 4959.

[28] The maximum specific rotation of (*R*)-**4** is $[\alpha]^{20}_{D}$ +68.9° (*c* 1, CHCl$_3$): Hayashi, T.; Konishi, M.; Kumada, M., unpublished results.

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# Low-Temperature Photochemistry of $(\eta^5\text{-C}_5\text{R}_5)\text{W(CO)}_3\text{CH}_2\text{SiMe}_2\text{H}$: Loss of Carbon Monoxide Followed by $\beta$-Hydrogen Transfer

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We report that near-UV irradiation of $(\eta^5\text{-C}_5\text{R}_5)\text{W(CO)}_3\text{CH}_2\text{SiMe}_2\text{H}$ (R = H, Me) at 77 or 196 K in hydrocarbon media results in loss of CO and the Si–H bond to give *cis*-$(\eta^5\text{-C}_5\text{R}_5)\text{W(CO)}_2(\text{H})(\text{CH}_2\text{SiMe}_2)$. Such a species has been proposed as an intermediate in the conversion represented by eq 1.[1] We

$$(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{CH}_2\text{SiMe}_2\text{H} \rightarrow (\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{SiMe}_3 \qquad (1)$$

undertook this study with the knowledge[2] that $(\eta^5\text{-C}_5\text{R}_5)\text{W(CO)}_3(\text{alkyl})$ complexes undergo light-induced loss of CO in rigid hydrocarbon media at low temperature to give spectroscopically detectable 16e$^-$ $(\eta^5\text{-C}_5\text{R}_5)\text{W(CO)}_2(\text{alkyl})$ complexes. For alkyl groups having $\beta$-H's, warm-up of the 16e$^-$ species yields *trans*-$(\eta^5\text{-C}_5\text{R}_5)\text{W(CO)}_2(\text{H})(\text{alkene})$ complexes.[2ab,e] We hoped to observe the related transfer of a $\beta$-H from a Si to the W atom. We chose to examine the W and not the Fe system in eq 1, because the alkene complex from $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{C}_2\text{H}_5$ is exceedingly labile.[3]

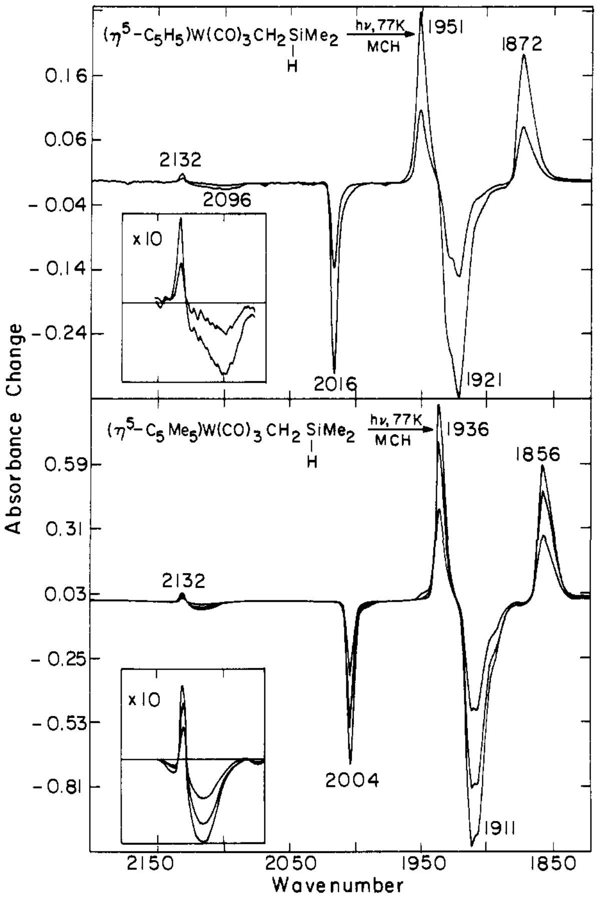

**Figure 1.** IR difference spectra (Nicolet 7199 FTIR) accompanying near-UV irradiation of ~1 mM $(\eta^5\text{-C}_5\text{R}_5)\text{W(CO)}_3\text{CH}_2\text{SiMe}_2\text{H}$ (top, R = H; bottom, R = Me) at 77 K in methylcyclohexane. The successive scans (greater optical changes) are for additional irradiation times to give ultimately ~50% consumption of starting material.

Figure 1 shows IR spectral changes accompanying near-UV irradiation of $(\eta^5\text{-C}_5\text{R}_5)\text{W(CO)}_3\text{CH}_2\text{SiMe}_2\text{H}$ at 77 K in a deoxygenated methylcyclohexane matrix.[4] Disappearance of the starting tricarbonyl is rapid and is associated with the dissociative loss of CO, as evidenced by the growth of absorption at 2132 cm$^{-1}$ due to uncomplexed CO.[5] The absorbance change at 2132 cm$^{-1}$ compared to the absorbance changes of the two bands in the CO stretching region of the starting tricarbonyl shows that one CO is generated per molecule of tricarbonyl consumed, within an experimental error of ~±20%.[6] It is noteworthy that the absorption associated with the Si–H bond (~2100 cm$^{-1}$) of the starting complex declines in a manner consistent with loss of one Si–H bond per CO molecule generated. In addition to the growth

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[6] A variety of metal carbonyls known to lose CO upon irradiation in rigid media have been examined under the same conditions to establish an extinction coefficient of ~300 M$^{-1}$ cm$^{-1}$ for CO in an alkane matrix. These results will be reported in a full paper.

0002-7863/83/1505-7768$01.50/0