The Reaction of Allene with Palladium(II) Acetate

Tadashi OKAMOTO, Yasumasa SAKAKIBARA* and Sango KUNICHIKA

Institute for Chemical Research, Kyoto University, Gokasho, Uji

* *Chemical Laboratory of Textile Fibers, Kyoto University of Industrial Arts and Textile Fibers, Kyoto*

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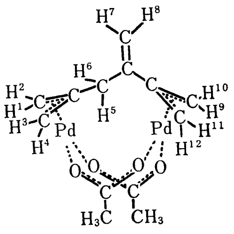
A recent note on the reaction of allene with π-allylpalladium(II) acetylacetonate to give 2,2'-bi-π-allyl complex of palladium[1] prompts us to report another bridged π-allyl complex obtained from allene and palladium acetate.

Palladium(II) acetate and allene were stirred in benzene at room temperature overnight; subsequent separation with a silica-gel column gave a yellow crystal, di-μ-acetato-[2,2'-(1-methyleneethylene)bis-π-allyl]dipalladium (I), in about a 20% yield. The structure of I was established by chemical and spectroscopic methods. Found: C, 34.63; H, 4.10%; mol wt (benzene, 37°C), 466. Calcd for $(C_3H_4)_3Pd_2(CH_3COO)_2$: C, 34.58; H, 4.11%; mol wt, 451. The hydrogenation of I gave 2,3,5-trimethylhexane and partially-hydrogenated products, 2,3,5-trimethyl-2-hexene and 2,4,5-trimethyl-2-hexene, which were determined by a study of the mass and NMR spectra. The NMR spectrum of I shows singlet absorptions at 5.67 (1H, H^7), 5.21 (1H, H^8), 3.95 (2H, H^{10} and H^{12}), 3.77 (2H, H^2 and H^4), 3.26 (2H, H^5 and H^6), 2.90 (2H, H^1 and H^3), 2.80 (2H, H^9 and H^{11}), and 2.05 ppm [(6H), acetoxy protons] at 100°C in acetic acid-d_4, with TMS used as the internal reference. At -28°C in deuterochloroform, the absorptions at 3.95, 3.26, and 2.90 ppm each separated into two peaks (Fig. 1). The couplings of the AB-type by H^5 and H^6 protons at the low temperature are not clear because of the disturbance by neighboring absorptions. The IR spectrum of I shows two broad absorptions, at 1570 and 1410 cm^{-1}, which can be assigned to the carboxylate ion. Acetate ligands were replaced, resulting in an insoluble complex, when I was treated with an aqueous sodium chloride solution.



(I)

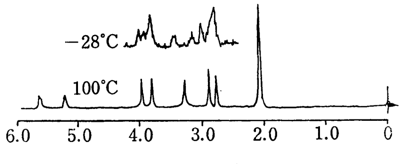
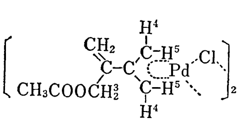


Fig. 1. NMR spectra of I.

An iron complex of a ligand with the same carbon skeleton was also obtained by Otsuka *et al.*[2] from hexacarbonyl 2,2'-bi-π-allyldiiron and allene. A similar route may be supposed for the formation of complex I, but no absorption due to 2,2'-bi-π-allylpalladium acetate was observed on the NMR spectrum of our reaction mixture.

When an aqueous sodium chloride solution was added to the reaction mixture, di-μ-chloro-bis-[2-(1-(acetoxymethyl)vinyl)-π-allyl]dipalladium(II) and di-μ-chloro-bis(2-acetoxy-π-allyl)dipalladium (III) were isolated from the solution in a total yield of 52%. The NMR spectrum of II shows singlet absorptions at 5.68 (1H, $=CH_2$), 5.46 (1H, $=CH_2$), 4.86 (2H, H^3), 4.18 (2H, H^4), 2.90 (2H, H^5) and 2.20 ppm (3H, acetoxy protons) in deuterochloroform at room temperature, with TMS used as the internal reference.



(II)

Although the mechanisms of these reactions are not yet clear, the newly-obtained complexes are the first examples of a stable complex obtained from palladium acetate.

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[1] R. P. Hughes and J. Powell, *J. Organometal. Chem.*, **20**, p. 17 (1969).

[2] S. Otsuka, A. Nakamura and K. Tani, Symposium on Organometallic Chemistry, Osaka, Japan, September, 1969, Abstract 25.