BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 1256—1257(1972)

The Addition of Ferrocenylpalladium Chloride to Conjugated Dienes

Akira KASAHARA and Taeko IZUMI

Department of Applied Chemistry, Faculty of Engineering, Yamagata University, Yonezawa-shi, Yamagata

(Received September 22, 1971)

The addition reactions of conjugated dienes with various transition-metal compounds have been studied by many workers. For example, cobalt hydrocarbonyl,[1] methyl or acetylcobalt tetracarbonyl,[2] manganese hydrocarbonyl,[3] methyl-manganese pentacarbonyl,[4] and palladium chloride[5] add to butadiene to form π-allyl metal complexes by way of 1,4 addition reactions. Furthermore, Heck[6] has reported that arylpalladium chlorides, prepared *in situ* from aryl-mercury compounds and lithium palladium chloride, react with conjugated dienes to form 1-arylmethyl-π-allyl-palladium chloride dimers in moderate yields. We have now found that ferrocenylpalladium chloride will also add to conjugated dienes.

The reactions of conjugated dienes with ferrocenylpalladium chloride, prepared *in situ* from ferrocenylmercuric chloride and lithium palladium chloride in acetonitrile, gave 1-ferrocenylmethyl-π-allylpalladium chloride derivatives, plus a small amount of biferrocenyl (III). The products were isolated by evaporating the solvent and by then chromatographing the crude products on alumina. Butadiene, isoprene, and 2,3-dimethylbutadiene all gave the expected π-allylpalladium chlorides (IIA, IIB, and IIC). However, the reaction of methyl sorbate with ferrocenylpalladium chloride resulted in the formation of methyl 5-ferrocenyl sorbate (IV); this reaction seems to proceed though the π-allylic intermediate (V). The evidence for the nature of the organic ligand in the binuclear π-allylic palladium chloride complexes comes from NMR and IR spectra, and the chloro-bridged binuclear structure for these compounds is supported by the conversion into the mononuclear acetylacetonate derivatives, pyridine derivatives, and triphenylphosphine derivatives.

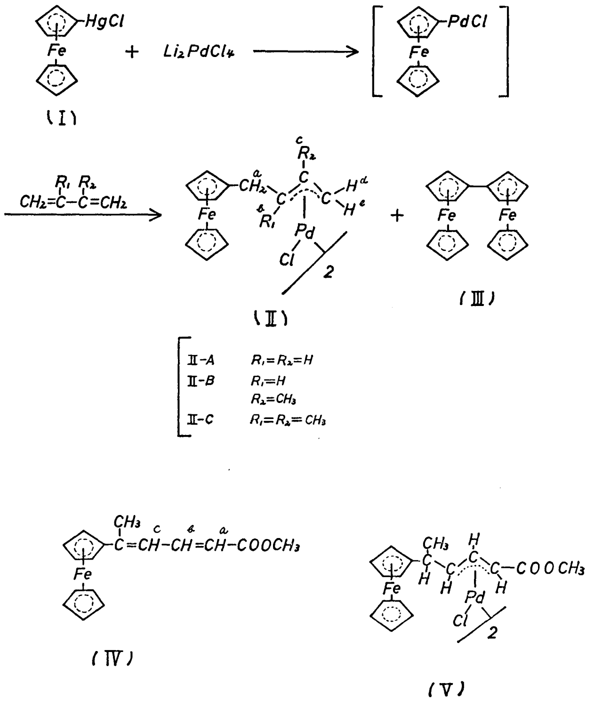

Fig. 1

---

[1] R. F. Heck and D. S. Breslow, *J. Amer. Chem. Soc.*, **83**, 1097 (1961).

[2] R. F. Heck, *ibid.*, **85**, 3381 (1963).

[3] W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Mutterties, and B. W. Howk, *ibid.*, **83**, 1601 (1961).

[4] W. D. Bannister, M. L. H. Green, and R. N. Haszeldine, *Proc. Chem. Soc.*, **1964**, 370.

[5] S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, **1963**, 4306.

[6] R. F. Heck, *J. Amer. Chem. Soc.*, **90**, 5542 (1968).

Experimental[7]

Materials. The ferrocenylmercuric chloride was prepared according to the method described by Fish and Rosenblum.[8]

The Preparation of Chloro-π-allylic Palladium Complexes. Lithium palladium chloride solutions were prepared by stirring 0.42 g (10 mmol) of anhydrous lithium chloride with 1.77 g (10 mmol) of anhydrous palladium chloride overnight at room temperature in 100 m*l* of acetonitrile. Into this lithium palladium chloride solution, a mixture of 4.20 g (10 mmol) of ferrocenylmercuric chloride and diolefins in a fourfold equivalent amount was then stirred at room temperature. In the reaction with butadiene, butadiene was added, by bubbling, to the reaction mixture under atmospheric pressure. The products were isolated by filtering to remove the solvent. The residue was dissolved in methylene chloride; subsequent recrystallization from ethanol afforded yellow crystals (mp 228—229°C, 6—10% yields), which were identified as biferrocenyl[9] by a comparison of the IR spectrum and by a mixed-melting-point determinations with an authentic sample. Further elution with methylene chloride and recrystallization from benzene-cyclohexane afforded the yellow product.

1-Ferrocenylmethyl-π-allylpalladium Chloride Dimer (II A). Mp 145—147°C (dec.). Yield, 35%. IR spectrum: 237, 255 cm^{-1} (Pd–Cl bridge). NMR sepctrum: 2.67 (d, $J=6.0$ Hz, H_a), 2.70 (d-d, $J=11.0$ and 0.3 Hz, H_e), 3.65 (d-d, $J=7.0$ and 0.3 Hz, H_d), 3.80 (d-t, $J=11.0$ and 6.0 Hz, H_b), 4.09 (s, ferrocene ring protons), 5.32 ppm (m, H_c).

Found: C, 44.22; H, 4.08%. Calcd for $C_{28}H_{30}Fe_2Pd_2Cl_2$: C, 44.12; H, 3.96%.

1-Ferrocenylmethyl-2-methyl-π-allylpalladium Chloride Dimer (II B). Mp 157—159°C (dec.). Yield, 24%. IR spectrum: 237, 255 cm^{-1} (Pd–Cl bridge). NMR spectrum: 2.11 (s, CH_3), 2.67 (d, $J=0.5$ Hz, H_e), 2.72 (d, $J=5.5$ Hz, H_a), 3.70 (d, $J=0.5$ Hz, H_d), 3.93 (t, $J=5.5$ Hz, H_b), 4.08 ppm (s, ferrocene ring protons). Found: C, 45.65; H, 4.45%. Calcd for $C_{30}H_{34}Fe_2Pd_2Cl_2$: C, 45.60; H, 4.33%.

1-Ferrocenylmethyl-1,2-dimethyl-π-allylpalladium Chloride Dimer (II C). Mp 127—129°C. Yield, 29%. IR spectrum: 237, 255 cm^{-1} (Pd–Cl bridge). NMR spectrum: 2.13 (s, CH_3 on the terminal carbon atom of the π-allyl group), 2.18 (s, CH_3 on the central carbon atom of the π-allyl group), 2.65 (d, $J=0.5$ Hz, H_e), 2.70 (s, H_a), 3.78 (d, $J=0.5$ Hz, H_d), 4.08 (s, ferrocene ring protons).

Found: C, 47.10; H, 4.77%. Calcd for $C_{32}H_{38}Fe_2Pd_2Cl_2$: C, 47.04; H, 4.68%.

The Preparation of π-Allylic Palladium Acetylacetonate Complexes. The corresponding chloro-complex (0.4 g) in benzene was mixed with a solution of thallium acetylacetonate (5% excess) in benzene and kept at room temperature for 30 min. After the thallous chloride had then been filtered off, the filtrate was evaporated to dryness; the residue was recrystallized from benzene - light petroleum to give pale yellow crystals.

1-Ferrocenylmethyl-π-allylpalladium Acetylacetonate. Mp 93—94°C (dec.). Found: C, 51.47; H, 5.01%. Calcd for $C_{19}H_{22}OFePd$: C, 51.31; H, 4.94%.

1-Ferrocenylmethyl-2-methyl-π-allylpalladium Acetylacetonate. Mp 140—141°C (dec.).

Found: C, 52.62; H, 5.38%. Calcd for $C_{20}H_{24}OFePd$: C, 52.36; H, 5.27%.

1-Ferrocenylmethyl-1,2-dimethyl-π-allylpalladium Acetylacetonate. Mp 69—70°C (dec.).

Found: C, 53.50; H, 5.65%. Calcd for $C_{21}H_{26}OFePd$: C, 53.35; H, 5.54%.

The Preparation of Chloro-(π-allyl)-pyridine-palladium Complexes. A solution of the chloro-bridged palladium complex (0.10 g) in methylene chloride was treated with a solution of pyridine (5% excess) in ether. After 10 min, the solvent was removed under reduced pressure; the residue was then recrystallized from benzene - cyclohexane to give pale yellow crystals.

Chloro-(1-ferrocenylmethyl-π-allyl)-pyridine Palladium. Mp 116—118°C (dec.).

Found: C, 49.81; H, 4.45; N, 3.17%. Calcd for $C_{19}H_{20}NFePdCl$: C, 49.59; H, 4.38; N, 3.04%.

Chloro-(1-ferrocenylmethyl-2-methyl-π-allyl)-pyridine Palladium. Mp 118—120°C (dec.).

Found: C, 50.83; H, 4.69; N, 3.11%. Calcd for $C_{20}H_{22}NFePdCl$: C, 50.65; H, 4.67; N, 2.97%.

Chloro-(1-ferrocenylmethyl-1,2-dimethyl-π-allyl)-pyridine Palladium. Mp 110—112°C.

Found: C, 51.70; H, 4.99; N, 2.98%. Calcd for $C_{21}H_{24}NFePdCl$: C, 51.66; H, 4.95; N, 2.86%.

The Preparation of Chloro-(π-allyl)-triphenylphosphine-palladium Complexes. To a solution of the chloro-bridged complex (0.10 g) in warm benzene (20 m*l*), a solution of triphenylphosphine (5% excess) in benzene was added; the resultant mixture was rapidly cooled to *ca.* 8°C. Pale yellow crystals were then filtered off and recrystallized from benzene - cyclohexane.

Chloro-(1-ferrocenylmethyl-π-allyl)-triphenylphosphine Palladium. Mp 142—144°C.

Found: C, 59.91; H, 4.79%. Calcd for $C_{32}H_{30}PFePdCl$: C, 59.73; H, 4.70%.

Chloro-(1-ferrocenylmethyl-2-methyl-π-allyl)-triphenylphosphine Palladium. Mp 103—105°C.

Found: C, 60.22; H, 5.13%. Calcd for $C_{33}H_{32}PFePdCl$: C, 60.29; H, 5.05%.

Chloro-(1-ferrocenylmethyl-1,2-dimethyl-π-allyl)-triphenylphosphine Palladium. Mp 107—109°C.

Found: C, 60.87; H, 5.21%. Calcd for $C_{34}H_{34}PFePdCl$: C, 60.82; H, 5.10%.

Methyl 5-Ferrocenyl Sorbate (IV). A mixture of 4.2 g (10 mmol) of ferrocenylmercuric chloride, 4.8 g (40 mmol) of methyl sorbate, and a lithium palladium chloride solution (prepared from 1.77 g of palladium chloride, 0.42 g of lithium chloride, and 100 m*l* of acetonitrile) was stirred at room temperature for 12 hr; the products were then isolated as in the preparation of chloro-π-allylic palladium complexes. The products were chromatographed on alumina. First elution with methylene chloride afforded yellow crystals (mp 228—229°C, 10% yields), which were identified as biferrocenyl. Further elution with methylene chloride and recrystallization from benzene - cyclohexane afforded yellow crystals (mp 44—45°C, 28% yields), which were identified as methyl 5-ferrocenyl sorbate on the basis of their IR and NMR spectra.

IR spectrum: 1712, 1641, 1620 cm^{-1}. NMR spectrum: 2.08 (s, CH_3), 3.69 (s, OCH_3), 4.05, 4.29, 4.40 (ferrocene ring protons) 5.80, 6.48, 7.68 ppm (ABX pattern, H_a, H_c, and H_b).

Found: C, 68.58; H, 5.81%. Calcd for $C_{17}H_{18}O_2Fe$: C, 68.56; H, 5.72%.

---

[7] All melting points are uncorrected. The NMR spectra were measured on a Hitachi H-60 spectrometer at 60 MHz in $CDCl_3$, using tetramethylsilane as the internal reference. The chemical shifts are given in ppm.

[8] R. Fish and M. Rosenblum, *J. Org. Chem.*, **30**, 1253 (1965).

[9] H. Shechter and J. H. Helling, *ibid.*, **26**, 1034 (1961).