The Palladium-catalyzed Ferrocenylation of Olefins

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Ferrocenylpalladium chloride, prepared *in situ* from chloromercuriferrocene and lithium chloropalladite, reacts readily with various olefins to produce alkenylferrocene derivatives. Enol esters and allylic alcohols also react to form (2-oxoalkyl)- and (3-oxoalkyl)-ferrocene derivatives. The synthesis of 1,1′-dialkenylferrocene derivatives from 1,1′-bis(chloromercuri)ferrocene, olefins and palladium salt is also reported. The reaction may proceed by means of a catalytic amount of the metal salt and by the aid of cupric chloride; it provides an extremely convenient method for the synthesis of a wide variety of ferrocene derivatives.

The reactions of olefins in the presence of transition metal compounds have been studied by many workers.[1] Recently, Heck[2] reported that the arylation of unsaturated compounds with Group VIII metal-aryl complexes has proved to be a generally applicable reaction. Several new useful synthetic organic reactions are based upon this arylation: olefinic arylation,[2a,g] aromatic haloethylation,[2c] aromatic allylation,[2e] and the synthesis of aldehydes or ketones with an aryl substituent on the α- or β- position by the arylation of allylic alcohols or enol esters.[2b,d] For example, "phenylpalladium chloride," prepared from phenylmercuric chloride and a palladium salt *in site*, reacts with ethylene to form styrene, hydrogen chloride, and palladium metal:

$$C_6H_5HgCl + PdCl_2 \rightleftharpoons [C_6H_5PdCl] + HgCl_2$$

$$[C_6H_5PdCl] + CH_2{=}CH_2 \longrightarrow C_6H_5CH{=}CH_2 + HCl + Pd$$

We have now found that, when Heck's reaction is carried out with ferrocenylpalladium salt prepared *in situ* from chloromercuriferrocene and a palladium salt the ferrocenyl group is introduced into the olefinic system.

Results and Discussion

In the presence of palladium salt, chloromercuriferrocene (**1**) was allowed to react with various olefins in polar solvents, such as methanol, ethanol, acetone, acetic acid, and acetonitrile. As with Heck's olefin arylation, the substitution reaction on the double bond has been observed to lead to the formation of 1-alkenylferrocenes, accompanied by a small amount of biferrocenyl (**2**). Moreover, 1,1′-bis(chloromercuri)ferrocene (**3**) reacts with olefins and palladium catalyst to form 1,1′-di(1-alkenyl)ferrocenes (**4**), accompanied by a small amount of bi-1,1′-ferrocenylene (**5**). The reactions carried out are summarized in Table 1. The properties of the products are given in Table 2.

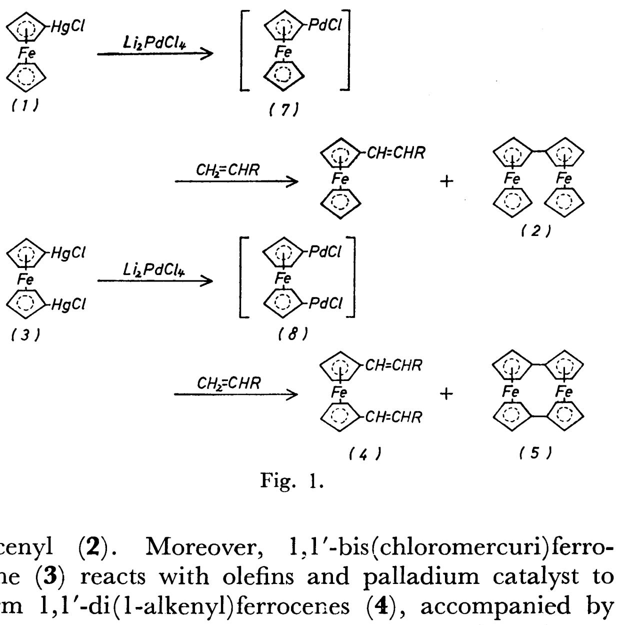
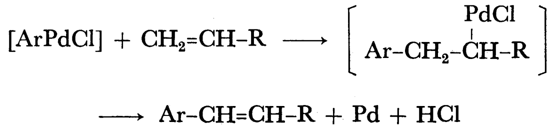


Fig. 1.

Furthermore, it was found that the reactions are generally initiated by a catalytic amount of palladium salt when cupric chloride is added to the reaction system. The latter has been to reoxidize the reduced palladium to the reactive Pd(II) form. Examples of catalytic ferrocenylation are given in Table 3.

The ferrocenylation of simple olefins, such as ethylene, styrene, and ethyl acrylate, resulted in the formation of vinylferrocene, styrylferrocene, and ethyl 3-ferrocenylacrylate respectively in moderate yields, accompanied by a small amount of **2**. In the olefinic palladium salt (**6**) from arylmercuric chloride and palladium salt, followed by the addition of **6** to the olefinic double bond and then the elimination of the hydride ion with palladium.

$$ArHgCl + PdCl_2 \rightleftharpoons \underset{(\mathbf{6})}{[ArPdCl]} + HgCl_2$$



$$[ArPdCl] + CH_2{=}CH{-}R \longrightarrow \left[Ar{-}CH_2{-}\overset{PdCl}{\overset{|}{C}H}{-}R \right] \longrightarrow Ar{-}CH{=}CH{-}R + Pd + HCl$$

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[1] C. W. Bird, "Transitional Metal Intermediates in Organic Synthesis," Logos Press, London (1966), p. 88; A. Guilo, "Advances in Organometallic Chemistry," Vol. 5, ed. by F. G. A. Stone and R. West, Academic Press, New York (1967), p. 321; E. W. Stern, "Catalysis Review," Vol. 1, ed. by H. Heineman, Marcel Dekker, Inc., New York (1968), p. 74; J. Tsuji, "Advances in Organic Chemistry, Methods and Results," Vol. 6, ed. by E. C. Taylor and H. Wynberg, Interscience Publishers, New York (1969), p. 109.

[2] a) R. F. Heck, *J. Amer. Chem. Soc.*, **90**, 5518 (1968); b) *ibid.*, **90**, 5526 (1968); c) *ibid.*, **90**, 5531 (1968); d) *ibid.*, **90**, 5535 (1968); e) *ibid.*, **90**, 5538 (1968); f) *ibid.*, **90**, 5542 (1968); g) *ibid.*, **91**, 6707 (1969).

TABLE 1. FERROCENYLATION OF OLEFINS

Olefin	Solvent	Product	Yield (%)[a]
(a) Reactions with chloromercuriferrocene (**1**).			
Ethylene	C_2H_5OH	Vinylferrocene (**10**)	45
		Biferrocenyl (**2**)	4
Styrene	CH_3OH	Styrylferrocene (**11**)	52
		Biferrocenyl (**2**)	3
Styrene	C_2H_5OH	Styrylferrocene (**11**)	50
		Biferrocenyl (**2**)	4
Styrene	CH_3COCH_3	Styrylferrocene (**11**)	45
		Biferrocenyl (**2**)	4
Styrene	CH_3COOH	Styrylferrocene (**11**)	47
		Biferrocenyl (**2**)	4
Styrene	CH_3CN	Styrylferrocene (**11**)	43
		Biferrocenyl (**2**)	6
Ethyl acrylate	C_2H_5OH	Ethyl 3-ferrocenylacrylate (**12**)	58
		Biferrocenyl (**2**)	3
Ethyl crotonate	C_2H_5OH	Ethyl 3-ferrocenylcrotonate (**13**)	52
		Biferrocenyl (**2**)	3
Methyl methacrylate	CH_3OH	Methyl 3-ferrocenylmethacrylate (**14**)	48
		Biferrocenyl (**2**)	5
Acrylonitrile	C_2H_5OH	3-Ferrocenylacrylonitrile (**15**)	49
		Biferrocenyl (**2**)	5
Acrolein	C_2H_5OH	3-Ferrocenyl-2-propenal (**16**)	45
		Biferrocenyl (**2**)	4
Methyl vinyl ketone	C_2H_5OH	4-Ferrocenyl-3-buten-2-one (**17**)	46
		Biferrocenyl (**2**)	7
Phenyl vinyl ketone	C_2H_5OH	3-Ferrocenyl-1-phenyl-2-propen-1-one (**18**)	45
		Biferrocenyl (**2**)	5
3-Buten-2-ol	C_2H_5OH	4-Ferrocenyl-2-butanone (**19**)	31
		Biferrocenyl (**2**)	9
2-Methyl-2-propenol	C_2H_5OH	2-Methyl-3-ferrocenylpropionaldehyde (**20**)	34
		Biferrocenyl (**2**)	6
5-Phenyl-2-cyclohexenol	CH_3CN	3-Ferrocenyl-5-phenylcyclohexanone (**21**)	14
		Biferrocenyl (**2**)	10
5,5-Dimethyl-2-cyclohexenol	CH_3CN	3-Ferrocenyl-5,5-dimethylcyclohexanone (**22**)	12
		Biferrocenyl (**2**)	12
Isopropenyl acetate	C_2H_5OH	α-Ferrocenylacetone (**23**)	27
		Biferrocenyl (**2**)	6
Acetophenone enol acetate	C_2H_5OH	α-Ferrocenylacetophenone (**24**)	16
		Biferrocenyl (**2**)	11
2-Methylallyl chloride	C_2H_5OH	3-Chloro-1-ferrocenyl-2-methylpropene (**25**)	21
		Biferrocenyl (**2**)	10
(b) Reaction with 1,1′-bis(chloromercuri)ferrocene (**3**)			
Styrene	C_2H_5OH	1,1′-Distyrylferrocene (**26**)	37
		Bi-1,1′-ferrocenylene (**5**)	6
Ethyl acrylate	C_2H_5OH	1,1′-Bis(2-ethoxycarbonylvinyl)ferrocene (**27**)	28
		Bi-1,1′-ferrocenylene(**5**)	8
Ethyl crotonate	C_2H_5OH	1,1′-Bis(2-ethoxycarbonyl-1-methylvinyl)ferrocene (**28**)	25
		Bi-1,1′-ferrocenylene (**5**)	10
Methyl methacrblate	C_2H_5OH	1,1′-Bis(2-methoxycarbonyl-2-methylvinyl)ferrocene (**29**)	31
		Bi-1,1′-ferrocenylene (**5**)	8
Acrylonitrile	C_2H_5OH	1,1′-Bis(2-cyanovinyl)ferrocene (**30**)	28
		Bi-1,1′-ferrocenylene (**5**)	11
Acrolein	C_2H_5OH	1,1′-Bis(2-formylvinyl)ferrocene (**31**)	22
		Bi-1,1′-ferrocenylene (**5**)	10
Methyl vinyl ketone	C_2H_5OH	1,1′-Bis(2-acetylvinyl)ferrocene (**32**)	27
		Bi-1,1′-ferrocenylene (**5**)	12
Phenyl vinyl ketone	C_2H_5OH	1,1′-Bis(2-benzoylvinyl)ferrocene (**33**)	25
		Bi-1,1′-ferrocenylene (**5**)	9

a) Yields are based upon the ferrocenylating agent.

TABLE 2. PROPERTIES AND ANALYSES OF FERROCENYLATION PRODUCTS

Compound	mp °C	Found, %		Calcd, %		IR Spectrum, (cm^{-1}) and NMR spectrum,[a] ppm (no. of protons)
		C	H	C	H	
10[b]	50—51	67.84	5.61	67.96	5.70	IR 1632, 987, 907.
11[c]	120—121	72.78	6.29	72.72	6.10	IR 1634, 960.
12[d]	74—75	63.22	5.48	63.40	5.67	IR 1710, 1620.
13[d]	69—71	64.38	6.01	64.45	6.08	IR 1712, 1618.
14	62—63	63.19	5.52	63.40	5.67	IR 1710, 1620. NMR 2.00 d (3) $-C{=}\overset{\mathbf{CH_3}}{C}-$ 3.73 s (3) $-COO\mathbf{CH_3}$ $\left.\begin{array}{l}4.08\ s\ (5)\\ 4.31\ q\ (2)\\ 4.41\ q\ (2)\end{array}\right\}$ ferrocene ring protons 7.40 q (1) $-\mathbf{CH}{=}C-$
15	80—81	65.68 (N, 5.87)	4.55	65.85 (N, 5.90)	4.63	IR 2170, 1612. NMR $\left.\begin{array}{l}4.14\ s\ (5)\\ 4.40\ s\ (4)\end{array}\right\}$ ferrocene ring protons 5.36 d (1) $-C{=}\mathbf{CH}-CN$ 7.22 d (1) $-\mathbf{CH}{=}C-CN$
16[e]	94—95	64.88	4.92	65.02	5.03	IR 1688, 1624.
17[f]	84—85	66.05	4.95	66.17	5.07	IR 1670, 1625.
18[g]	136—137	72.07	5.38	72.17	5.55	IR 1660, 1607.
19[h]	45—46	65.49	6.18	65.66	6.29	IR 1715.
27	53—55	65.55	6.24	65.66	6.29	IR 2850, 1718. NMR 1.18 d (3) $-\mathbf{CH_3}$ 2.84 d (2) $-\mathbf{CH_2}-$ 3.98 m (1) $-\mathbf{CH}-$ 4.12 s (9) ferrocene ring protons 9.74 d (1) $-\mathbf{CHO}$
21	71—72	73.66	6.06	73.75	6.18	IR 1710. NMR 2.10—3.30 m (8) cyclohexanone ring protons 4.11 s (9) ferrocene ring protons 7.28 s (5) phenyl protons
22	89—90	67.08	7.71	67.15	7.74	IR 1710. NMR 0.99 s (3) $-\mathbf{CH_3}$ 1.08 s (3) $-\mathbf{CH_3}$ 1.98—3.24 m (7) cyclohexanone ring protons 4.13 s (9) ferrocene ring protons
23	46—47	64.81	5.80	64.95	5.86	IR 1713. NMR 2.21 s (3) $-\mathbf{CH_3}$ 3.92 s (2) $-\mathbf{CH_2}-$ 4.12 s (9) ferrocene ring protons
24[c]	80—81	68.43	5.69	68.56	5.75	IR 1687.
25	105—106	59.26	5.61	59.35	5.74	IR 1635, 805. NMR 1.48 d (3) $-\overset{\mathbf{CH_3}}{C}{=}C-$ 2.87 d (2) $-\mathbf{CH_2}Cl$ 4.12 s (9) ferrocene ring protons 7.31 m (1) $-\mathbf{CH}{=}C-$
26[i]	166—168	79.87	5.63	79.99	5.68	IR 1630, 961.
27	83—84	62.88	5.91	62.83	5.80	IR 1710, 1618. NMR 1.33 t (6) $-COOCH_2\mathbf{CH_3}$ 4.33 d (4) $-COO\mathbf{CH_2}CH_3$ 4.55 s (8) ferrocene ring protons 6.01 d (2) $-C{=}\mathbf{CH}-COOEt$ 7.52 d (2) $-\mathbf{CH}{=}C-COOEt$
28	65—66	64.25	6.31	64.38	6.38	IR 1711, 1620. NMR 1.26 t (6) $-COOCH_2\mathbf{CH_3}$ 1.98 d (6) $\mathbf{CH_3}-CH{=}C-$ 4.20 q (4) $-COO\mathbf{CH_2}CH_3$

Compound	mp °C	Found, %		Calcd, %		IR Spectrum, (cm^{-1}) and NMR spectrum,[a)] ppm (no. of protons)
		C	H	C	H	
						4.38 m(4) 4.53 m(4) } ferrocene ring protons 6.04 q (2) -C=**CH**-COOEt
29	96—97	62.95	5.92	62.83	5.80	IR 1710, 1624. NMR 2.01 d (6) -C=C-**CH$_3$** 3.77 s (6) -COO**CH$_3$** 4.37 m(4) 4.48 m(4) } ferrocene ring protons 7.45 q (2) -**CH**=C-COOCH$_3$
30	101—102	66.78 (N% 9.76)	4.25	66.64 (N% 9.71)	4.19	IR 2170, 1616. NMR 4.42 s (8) ferrocene ring protons 5.39 d (2) -C=**CH**-CN 7.31 d (2) -**CH**=C-CN
31	69—70	65.73	4.21	65.76	4.14	IR 2810, 1687, 1620. NMR 4.39 s (8) ferrocene ring protons 5.43 d (2) -C=**CH**-CHO 7.38 d (2) -**CH**=C-CHO 9.61 d (2) -**CHO**
32	112—113	67.21	5.78	67.08	5.62	IR 1685, 1617. NMR 2.29 s (6) -**CH$_3$** 4.47 s (8) ferrocene ring protons 6.34 d (2) -C=**CH**-COCH$_3$ 7.46 d (2) -**CH**=C-COCH$_3$
33	145—146	75.44	5.05	75.33	4.96	IR 1680, 1619. NMR 4.49 s (8) ferrocene ring protons 5.57 d (2) -C=**CH**-COPh 7.71 d (2) -**CH**=C-COPh 7.28 s (10) phenyl protons

a) 60 Mc with TMS as internal standard in CDCl$_3$ solution.
b) M. D. Rausch and A. Siegel, *J. Organometal. Chem.* **11**, 317 (1968).
c) P. L. Pauson and E. E. Watts, *J. Chem. Soc.*, **1963**, 2990.
d) P. Da Re and E. Sianesi, *Expirientia*, **21**, 648 (1966).
e) K. Schloegl and H. Egger, *Ann.*, **676**, 76 (1964).
f) J. M. Osgerby and P. L. Pauson, *J. Chem. Soc.*, **1961**, 4604.
g) C. R. Hauser and J. K.Lindsay, *J. Org. Chem.*, **23**, 906 (1957).
h) J. Decombe, J. P. Ravoux, and A. Dormond, *Compt. rend.*, **258**, 2348 (1964).
i) K. Sonogashira and N. Hagihara,*Kogyo Kagaku Zasshi*, **66**, 1090 (1963).

TABLE 3. CATALYTIC FERROCENYLATION OF OLEFINS WITH CHLOROMERCURIFERROCENE (**1**).

Olefin	Solvent	Product	Yield(%)[a)]
Styrene	C$_2$H$_5$OH	**11**	44
		2	12
Ethyl acrylate	C$_2$H$_5$OH	**12**	41
		2	10
Ethyl crotonate	C$_2$H$_5$OH	**13**	36
		2	11
Methyl methacrylate	CH$_3$OH	**14**	38
		2	9
Methyl vinyl ketone	C$_2$H$_5$OH	**17**	31
		2	11
Phenyl vinyl ketone	C$_2$H$_5$OH	**18**	37
		2	8
Acrylonitrile	C$_2$H$_5$OH	**15**	33
		2	10

a) Yields are based upon the ferrocenylating agent used.

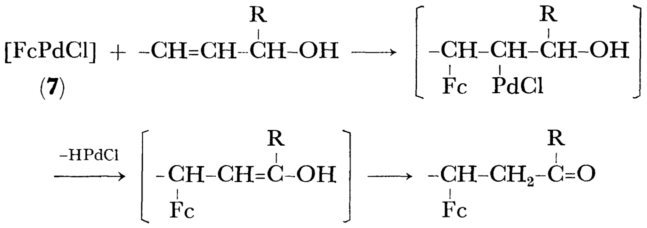
In the reactions of olefins with **1** and palladium salt, a δ-bonded ferrocenylpalladium compound (**7**) will function as the ferrocenylation agent, just as arylpalladium salt (**6**) in Heck's arylation reaction. The formation of **2** probably results from a coupling reaction of **7** or from a reaction of **7** with **1**. Similarly, the reactions of olefins with **3** and palladium salt may involve the formation of 1,1′-bis(chloropalladium)ferrocene (**8**) and the mechanism of the formation of **5** as a by-product involves a coupling reaction of **8** or a reaction of **8** with **3**.

$$\underset{(\mathbf{1})}{\mathrm{FcHgCl}} + \mathrm{PdCl_2} \rightleftarrows \underset{(\mathbf{7})}{[\mathrm{FcPdCl}]} + \mathrm{HgCl}$$

$$\underset{(\mathbf{7})}{2[\mathrm{FcPdCl}]} \longrightarrow \underset{(\mathbf{2})}{\mathrm{Fc\text{-}Fc}} + \mathrm{PdCl_2} + \mathrm{Pd}$$

$$\underset{(\mathbf{7})}{[\mathrm{FcPdCl}]} + \underset{(\mathbf{1})}{\mathrm{FcHgCl}} \longrightarrow \underset{(\mathbf{2})}{\mathrm{Fc\text{-}Fc}} + \mathrm{HgCl_2} + \mathrm{Pd}$$

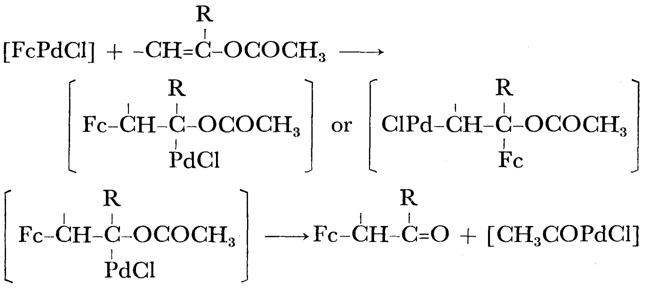
The ferrocenylation of allylic alcohols led to the formation aldehydes or ketones with a ferrocenyl substituent at the β-position. For example, 2-methyl-2-propenol, 5-phenyl-2-cyclohexenol, and 5,5-dimethyl-2-cyclohexenol reacted with **1** in the presence of palladium salt to produce 2-methyl-3-ferrocenylpropionaldehyde, 3-ferrocenyl-5-phenylcyclohexanone, and 3-ferrocenyl-5, 5-dimethylcyclohexanone respectively. These result suggest that the mechanism of the ferrocenylation of allylic alcohol involves the addition of **7** to the allylic double bond, and then hydride elimination from the hydroxylsubstituted carbon:



$$\underset{(\mathbf{7})}{[\mathrm{FcPdCl}]} + \mathrm{-CH{=}CH-}\overset{\mathrm{R}}{\mathrm{C}}\mathrm{H-OH} \longrightarrow \left[\mathrm{-}\underset{\mathrm{Fc}}{\mathrm{CH}}\mathrm{-}\underset{\mathrm{PdCl}}{\mathrm{CH}}\mathrm{-}\overset{\mathrm{R}}{\mathrm{C}}\mathrm{H-OH}\right]$$

$$\xrightarrow{-\mathrm{HPdCl}} \left[\mathrm{-}\underset{\mathrm{Fc}}{\mathrm{CH}}\mathrm{-CH{=}}\overset{\mathrm{R}}{\mathrm{C}}\mathrm{-OH}\right] \longrightarrow \mathrm{-}\underset{\mathrm{Fc}}{\mathrm{CH}}\mathrm{-CH_2-}\overset{\mathrm{R}}{\mathrm{C}}\mathrm{{=}O}$$

In addition, isopropenyl acetate and acetophenone enol acetate reacted with **1** and palladium salt to yield α-ferrocenylacetone and α-ferrocenylacetophenone respectively. These results suggest that the mechanism of the ferrocenylation of the enol ester involves an addition-elimination sequence; the addition of the ferrocenyl group preferentially occurs on the less substituted carbon atom, followed by the elimination of palladium with an acyl group to produce a carbonyl compound:

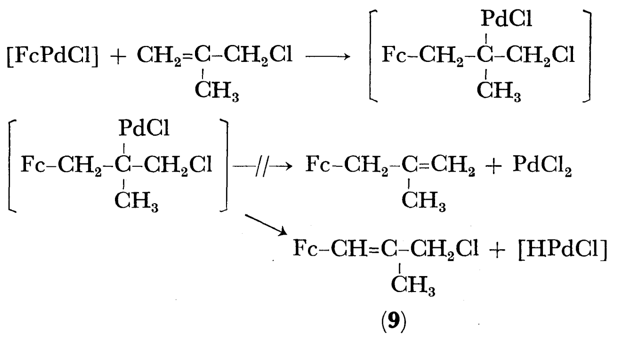


$$[\mathrm{FcPdCl}] + \mathrm{-CH{=}}\overset{\mathrm{R}}{\mathrm{C}}\mathrm{-OCOCH_3} \longrightarrow$$

$$\left[\mathrm{Fc-CH-}\underset{\mathrm{PdCl}}{\overset{\mathrm{R}}{\mathrm{C}}}\mathrm{-OCOCH_3}\right] \text{ or } \left[\mathrm{ClPd-CH-}\underset{\mathrm{Fc}}{\overset{\mathrm{R}}{\mathrm{C}}}\mathrm{-OCOCH_3}\right]$$

$$\left[\mathrm{Fc-CH-}\underset{\mathrm{PdCl}}{\overset{\mathrm{R}}{\mathrm{C}}}\mathrm{-OCOCH_3}\right] \longrightarrow \mathrm{Fc-CH-}\overset{\mathrm{R}}{\mathrm{C}}\mathrm{{=}O} + [\mathrm{CH_3COPdCl}]$$

Heck[2c] reported that the reaction of arylpalladium salts with allylic halides produces the allylated aromatic compounds. For example, phenylpalladium salts react with allyl chloride and 2-methylallyl chloride to produce allylbenzene and (2-methylallyl)benzene respectively. He also suggested that this allylation reaction involves the addition of the arylpalladium chloride to the allylic double bond and the elimination of palladium chloride rather than of palladium hydride chloride. However, the reaction of **1** with 2-methylallyl chloride led to the formation of 3-chloro-1-ferrocenyl-2-methylpropene (**9**). This result suggests that the mechanism of the formation of **9** involves the elimination of palladium with a neighboring hydrogen rather than with chlorine.



$$[\mathrm{FcPdCl}] + \mathrm{CH_2{=}}\underset{\mathrm{CH_3}}{\mathrm{C}}\mathrm{-CH_2Cl} \longrightarrow \left[\mathrm{Fc-CH_2-}\underset{\mathrm{CH_3}}{\overset{\mathrm{PdCl}}{\mathrm{C}}}\mathrm{-CH_2Cl}\right]$$

$$\left[\mathrm{Fc-CH_2-}\underset{\mathrm{CH_3}}{\overset{\mathrm{PdCl}}{\mathrm{C}}}\mathrm{-CH_2Cl}\right] \not\longrightarrow \mathrm{Fc-CH_2-}\underset{\mathrm{CH_3}}{\mathrm{C}}\mathrm{{=}CH_2} + \mathrm{PdCl_2}$$

$$\searrow \underset{(\mathbf{9})}{\mathrm{Fc-CH{=}}\underset{\mathrm{CH_3}}{\mathrm{C}}\mathrm{-CH_2Cl}} + [\mathrm{HPdCl}]$$

Experimental

Analysis and Materials. All the melting points are uncorrected. The IR spectra were measured on KBr disks with a Hitachi EPI-S2 spectrometer, and the NMR spectra were obtained by means of a Hitachi H-60 spectrometer in $CDCl_3$, using tetramethylsilane as the internal standard.

Chloromercuriferrocene (**1**) and 1,1′-bis(chloromercuri) ferrocene (**3**) were prepared according to the method described by Fish and Rosenblum.[3] 3-Buten-2-ol,[4] phenyl vinyl ketone,[5] and acetophenone enol acetate[6] were synthesized according to known procedures. 5-Phenyl-2-cyclohexenol and 5,5-dimethyl-2-cyclohexenol were synthesized by the lithium-auminum-hydride reduction of 5-phenyl-2-cyclohexenone and 5,5-dimethyl-2-cyclohexenone respectively. The other olefins were of a commercial grade and were purified before use.

General Procedure for the Ferrocenylation of Olefins. Lithium chloropalladite solutions were prepared by stirring 0.84 g (20 mmol) of anhydrous lithium chloride and 1.77 g (10 mmol) of anhydrous palladium chloride overnight at room temperature in 100 m*l* of the respective solvent expect in the case of acetonitrile, where 10 mmol instead of 20 mmol of lithium chloride was used. To this lithium chloropalladite solution, except in the reaction with ethylene, a mixture of 4.20 g (10 mmol) of **1** and four times as much olefin was added, after which the mixture was stirred at room temperature for 12 hr. In the case of the reaction with ethylene, ethylene was bubbled into the reaction mixture under atmospheric pressure. The products were isolated by filtration to remove any precipitated palladium and by distillation under reduced pressure to remove the solvent. The residue was dissolved in benzene; chromatograph on alnmina afforded yellow crystals (mp 228—229°C, 2.12% yields) which were identified as biferrocenyl (**2**)[7] by a comparison of the IR spectra and by a mixed-melting-point determination. Further elution with benzene and recrystallization from methanol, ethanol, or benzene-cyclohexane afforded the respective ferrocenylation product. The structures of the products were confirmed by a mixed-melting-point determinations with an authentic sample and by observation of the IR and NMR spectra. The results are summarized in Table 1, while the analytical results and the properties of the products are listed in Table 2.

In the reactions with **3**, 3.28 g (5 mmol) of **3** and four times olefin as much were added to a lithium chloropalladite solution prepared from 0.84 g of lithium chloride and 1.77 g of palladium chloride; the reactions were then carried out in the manner described above. The crude product was dissolved in benzene and chromatographed on alumina. First, elution with benzene afforded deep yellow crystals (mp 370°C), which were identical as bi-1,1′-ferrocenylene (**5**)[8] by a comparison of the IR and NMR spectra with those of an authentic sample. Further elution with benzene or chloroform afforded 1,1′-divinylferrocene derivatives (**4**). The structures of the products were confirmed by a mixed-melting-point determination with an authentic sample and by observation of the IR and NMR spectra. The results and the

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3) R. E. Fish and M. Rosenblum, *J. Org. Chem*, **30**, 1253 (1965).

4) W. G. Young, S. Winstein, and A. N. Prater, *J. Amer. Chem. Soc.*, **58**, 289 (1936).

5) W. G. Young and J. D. Roberts, *ibid.*, **68**, 649 (1946).

6) P. Z. Bedoukian, *ibid.*, **67**, 1430 (1745).

7) H. Shechter and J. H. Helling, *J. Org. Chem.*, **26**, 1034 (1961).

8) F. L. Hedberg and H. Rosenbeg, *J. Amer. Chem. Soc.*, **91**, 1258 (1969): M. D. Rausch, R. F. Kovar, and C. S. Kraihauzel, *ibid.*, **91**, 1259 (1969).

properties of the products are also listed in Tables 1 and 2.

In catalytic reactions, 3.4 g (20 mmol) of cupric chloride dihydrate, 4.2 g (10 mmol) of **1**, and four times olefin as much were added to a lithium chloropalladite solution prepared from 0.17 g (1 mmol) of palladium chloride, 0.08 g (2 mmol) of lithium chloride, and 100 m*l* of ethanol or methanol: the reactions were then carried out in the manner described above. The results are given in Table 3.

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