(cymmetrical multiplets of total relative areas of 8 from the ethyl groups), and at −6.78 ppm (narrow multipet of relative area 1 from the aromatic proton).

Reaction of Cupric Chloride with Benzylmercuric Chloride. A solution of 0.19 g (1 mmol) of dibenzylmercury, 0.14 g (1 mmol) of mercuric chloride, 0.042 g (1 mmol) of lithium chloride, and 1.0 ml of acetic acid was stirred for 5 min to form benzylmercuric chloride. Then 0.1 ml of water and 0.27 g (2 mmol) of cupric chloride were added, and the mixture was stirred magnetically for 2 days at room temperature. At the end of this time, gas chromatographic analyses showed that the solution was 0.80 *M* in benzyl chloride and that there was also a small amount of benzyl acetate present. The same results were obtained when 0.1 ml of 0.1 *M* lithium palladium chloride in acetic acid was also added and when it and 40 psig of ethylene were present.

Acknowledgments. The author gratefully acknowledges the assistance of Mr. Joseph Keelins with the experimental work. The nmr spectra were kindly measured by Dr. M. M. Anderson of these laboratories.

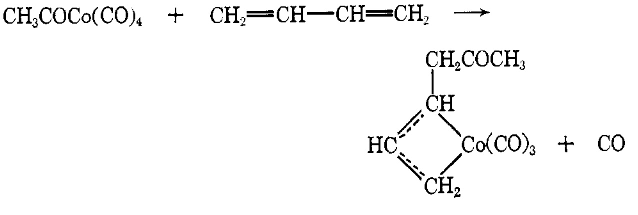
The Addition of Alkyl- and Arylpalladium Chlorides to Conjugated Dienes

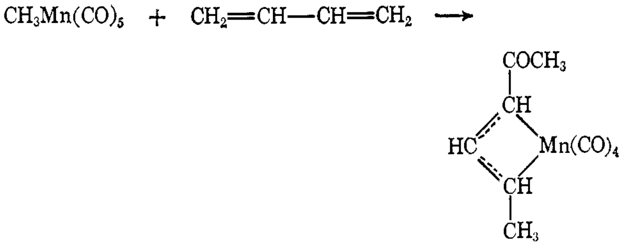
R. F. Heck

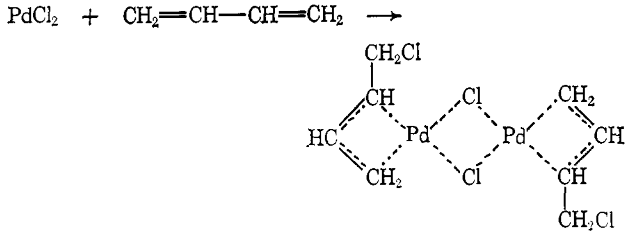
Contribution from the Research Center of Hercules Inc.,
Wilmington, Delaware 19899.
Received December 7, 1967

Abstract: Aryl- and certain alkylpalladium chlorides, prepared *in situ* from aryl- or alkylmercury or -tin compounds and lithium palladium chloride, react readily with conjugated dienes to form 1-arylmethyl or 1-alkyl-π-allylpalladium chloride dimers, in low to moderate yields. A catalytic synthesis of arylbutenyl acetates from a conjugated diene, an arylmercuric salt, and lead tetraacetate with a catalytic amount of palladium acetate is also reported.

Addition reactions of various transition metal carbonyl derivatives to conjugated dienes are well known. Cobalt hydrocarbonyl,[1] manganese hydrocarbonyl,[2] and nitrosylironcarbonyl hydride[3] add to butadiene to form 1-methyl-π-allylmetal complexes, all apparently by way of 1,4-addition reactions to form σ-bonded 2-butenylmetal compounds which then cyclize to the π complexes. Methyl- or acetylcobalt tetracarbonyl reacts with butadiene to form 1-acetylmethyl-π-allylcobalt tricarbonyl.[4] Methylmanganese pentacarbonyl reacts similarly with butadiene, but a rearrangement occurs producing 1-acetyl-3-methyl-π-allylmanganese tetracarbonyl.[5] Similar reactions of *noncarbonyl transition metal alkyls* have not been reported although there is one example of the addition of a chloride. Palladium chloride and butadiene form 1-chloromethyl-π-allylpalladium chloride dimer.[6] We have now found that certain alkyl- and arylpalladium chlorides will also add to conjugated dienes.







Results

Alkyl- and arylpalladium chlorides are generally unstable materials. In the present investigation they were prepared by exchange reactions between lithium palladium chloride and alkyl- or arylmercury or -tin compounds in acetonitrile solution, in the presence of the conjugated dienes. Reactions were rapid at room temperature and the products were isolated by evaporating the solvent and chromatographing the crude products on alumina. In the examples tried, yellow crystalline products were isolated in low to moderate yields which, by analyses and nmr spectral studies, proved to be 1-alkyl- or 1-arylmethyl-π-allylpalladium chloride dimers. Only methyl-, benzyl-, and arylpalladium chlorides have been investigated because alkyls with β-hydrogen atoms are very unstable with respect to chloropalladium hydride and olefin and probably would not react rapidly enough with dienes

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

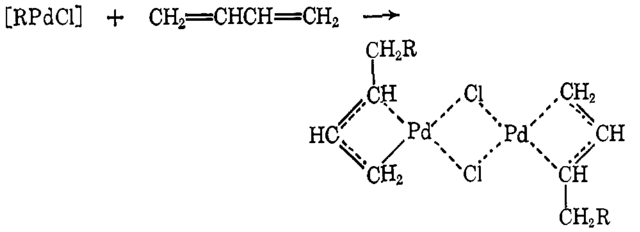
[2] W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Howk, *ibid.*, **83**, 1601 (1961).

[3] R. Bruce, F. M. Chaudhary, G. R. Knox, and P. L. Pauson, *Z. Naturforsch.*, 20b, 73 (1965).

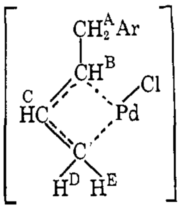
[4] R. F. Heck, *J. Amer. Chem. Soc.*, **85**, 3381 (1963).

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

[6] B. L. Shaw, *Chem. Ind.* (London), 1190, (1962).



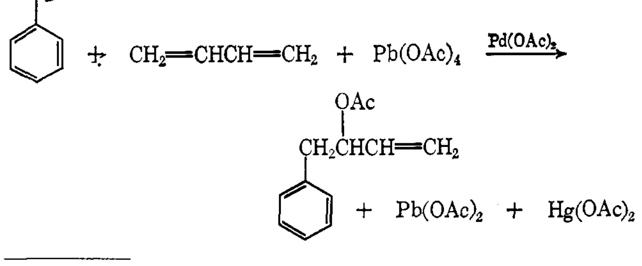
to give appreciable yields of the adducts. Butadiene, isoprene, and 1,3-cyclohexadiene all gave the expected π-allylpalladium chlorides. The products prepared, their properties, and analyses are given in Table I. The nmr spectra of the compounds are given in Table II.



Presumably, bis-π-allylpalladium derivatives could be obtained by the addition of a second alkyl or aryl group to a π-allylpalladium derivative, followed by reaction with 1 additional mol of a diene. This reaction has not been observed; instead, various coupling reactions take place. For example, even in the presence of a diene, 1-methyl-π-allylpalladium chloride dimer reacts with diphenylmercury to produce mainly crotylbenzene and biphenyl.

The addition of alkyl- or arylpalladium chlorides to dienes probably involves *cis*, covalent addition, either 1,2 or 1,4 to the diene system, followed by a rapid cyclization to form a π-allyl complex. An alternative but less likely mechanism involves the direct carbon alkylation or arylation of a 1-chloromethyl-π-allylpalladium chloride dimer, formed first from the palladium chloride and the diene. Presumably, other π-allylpalladium salts than the chloride could be prepared by the same procedure provided some ligand is present to complete the coordination sphere of the palladium if a halogen bridge cannot be formed. A few attempts to prepare π-allyl derivatives from rhodium, ruthenium, platinum, and iron chlorides by the same procedure have been unsuccessful.

The fact that π-allylpalladium salts are decomposed into allylic acetates by lead tetraacetate[7] led us to attempt a catalytic synthesis of arylbutenyl acetates from arylmercuric salts, butadiene, and lead tetraacetate with a catalytic amount of palladium acetate. The reaction succeeded and a 78% yield of 1-phenyl-3-buten-2-yl acetate was obtained from phenylmercuric acetate and butadiene. Lead tetraacetate, therefore, appears to be another reagent which can reoxidize palladium metal to palladium(II). None of the allylic isomer, 1-phenyl-2-buten-4-yl acetate, was found. The absence of the primary allylic acetate suggests that the reaction may not go through the π-allylpalladium salt but that oxidation may occur at the 1:2 σ adduct stage but more work is necessary to establish if the primary isomer would have survived if it had been present. A similar reaction using *p*-anisylmercuric acetate produced a 3:1 mixture of the secondary and primary *p*-anisylbutenyl acetates in 45% yield. Under the same reaction conditions, isoprene reacted only with lead tetraacetate producing 1,2-diacetoxy-2-methyl-3-butene.



That lead tetraacetate will react with σ-bonded organopalladium compounds as well as with π-allylpalladium complexes is shown by the fact that inclusion of lead tetraacetate in a reaction mixture of phenylmercuric acetate and ethylene with a catalytic amount of lithium palladium chloride led to the formation of 16% β-phenethyl acetate along with 19% styrene. Similarly at 50°, phenylmercuric acetate with propylene and a palladium acetate catalyst gave 14% 1-phenyl-2-propyl acetate and 9% *trans*-1-phenyl-1-propene.

$$C_6H_5HgOAc + CH_2{=}CH_2 + Pb(OAc)_4 \xrightarrow{LiPdCl_3}$$
$$C_6H_5CH_2CH_2OAc + C_6H_5CH{=}CH_2 + Hg(OAc)_2 + Pb(OAc)_2$$

Experimental Section

Lithium Palladium Chloride Solutions. Acetonitrile was dried by passage over molecular sieves. Solutions 0.1 *M* in $LiPdCl_3$ were prepared by stirring the appropriate amount of anhydrous palladium chloride (Engelhard Industries) with 2 equiv of lithium chloride overnight in dry acetonitrile. Only 1 mol of lithium chloride dissolves per mole of palladium chloride.

1-Benzyl-π-allylpalladium Chloride Dimer. In a heavy-walled Pyrex bottle were placed 0.62 g (2 mmol) of phenylmercuric chloride (Aldrich Chemical Co.) and a magnetic stirring bar. The bottle was capped with a butyl rubber line metal cap. The mixture was stirred and 6 ml of liquid butadiene and 20 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile were injected in that order through a small hole in the metal cap and through the rubber liner. The mixture was stirred at room temperature overnight and volatile material was distilled at room temperature under reduced pressure. The residue was dissolved in methylene chloride and chromatographed on neutral alumina. The yellow product was eluted with 1% methanol in methylene chloride. After evaporation of the solvent at room temperature under reduced pressure, the crude product was recrystallized from ether by adding pentane. Yellow crystals were obtained weighing 0.26 g (48%).

1-Benzyl-2-methyl-π-allylpalladium Chloride Dimer. A reaction was carried out as above employing 4 ml of isoprene instead of 6 ml of butadiene. Isolation and recrystallization of the product in the same way yielded 0.32 g (56%) of pale yellow crystals.

1-Benzyl-3-methyl-π-allylpalladium Chloride Dimer. A mixture of 1.86 g (6 mmol) of phenylmercuric chloride, 12 ml of *trans*-piperylene, and 60 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile was stirred at room temperature for 3 days and the product was isolated as in the preceding examples. Recrystallization from methylene chloride by adding pentane gave 0.35 g (20%) of yellow crystals, mp 177.0–177.5° dec.

cis-Piperylene gave the same product in the above reaction, in 28% yield.

1-Ethyl-π-allylpalladium Chloride Dimer. The reactants, 0.75 g (3 mmol) of methylmercuric chloride, 8 ml of liquid butadiene, and 30 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile solution, were stirred for 3 hr at 40° and at room temperature overnight. Isolation of the product as above, followed by three recrystallizations of the product from methylene chloride by adding pentane, gave 0.20 g (30%) as clusters of yellow needles.

1-[2-(1-Naphthyl)ethyl]-π-allylpalladium Chloride Dimer. A reaction mixture of 1.13 g (3 mmol) of 1-chloromercurimethylnaph-

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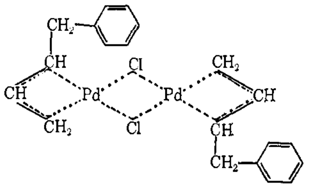
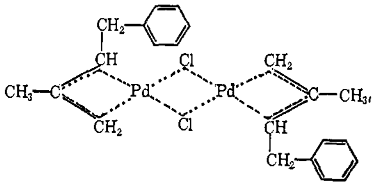
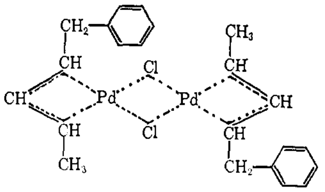
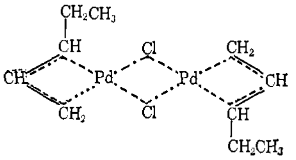
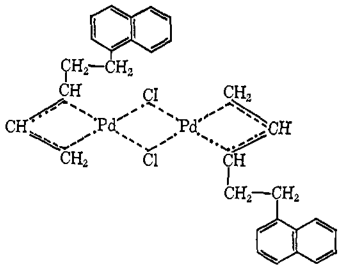
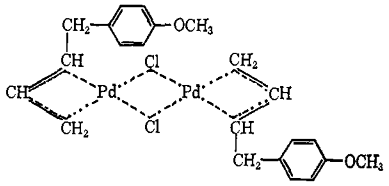
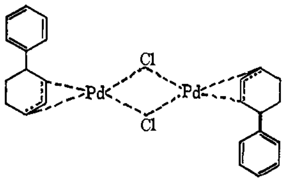
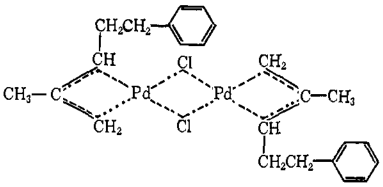
(7) S. Winstein, personal communication.

Table I. New π-Allylpalladium Chloride Complexes

Compound	Mp, °C	Found, %			Calcd, %		
		C	H	Cl	C	H	Cl
	135–136	43.81	4.23	13.98	43.98	4.06	12.99
	158.5–159.5	45.96	4.86		46.02	4.56	
	177.0–177.5	45.61	4.88		46.02	4.56	
	74.8–76.2	28.62	4.71		28.46	4.30	
	178.4–179.8 dec	53.09	4.71		53.44	4.48	
	150.8–151.2	42.54	4.41		43.59	4.32	
	110–111 dec	47.85	4.59		48.19	4.38	
	169.5–170.5 dec	48.81	5.35		47.86	5.02	

thalene,[8] 8 ml of butadiene, and 30 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile solution was stirred at room temperature overnight. Isolation of the product as in the examples above, and three recrystallizations by dissolving in methylene chloride and adding pentane, gave 0.090 g of a yellow powder.

1-*p*-Anisylmethyl-π-allylpalladium Chloride Dimer. A reaction mixture containing 3.42 g (10 mmol) of *p*-chloromercurianisole,[9]

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[8] O. Grummitt and A. C. Buck, *J. Amer. Chem. Soc.*, **65**, 295 (1943).

Table II. Nmr Spectra of π-Allylpalladium Chloride Dimers

Compound	Absorption,[a] ppm							
	H_A	H_B	H_C	H_D	H_E	CH_3	Aromatic	Other
1-Benzyl-π-allylpalladium chloride dimer	−3.47, doublet $J = 5.9$	−4.53, quintet	−5.78, double triplet, $J_1 = 6.8, J_2 = J_3 = 11.3$	−4.30, doublet, $J = 6.2$	−3.31, doublet, $J = 11.3$	...	−7.15, singlet	...
1-Benzyl-2-methyl-π-allylpalladium chloride dimer	−3.50, multiplet	−4.17		−4.17	−3.12, singlet	−2.51, singlet	−7.64, singlet	...
1-Benzyl-3-methyl-π-allylpalladium chloride dimer	−2.98, doublet, $J = 6.5$	−3.60 to −4.00,[b] multiplet	−5.14, doublet, $J_1 = J_2 = 11$	...	−3.60 to −4.00[b]	−1.25, doublet, $J = 6.5$	−7.31, singlet	
1-Ethyl-π-allylpalladium chloride dimer	−2.12, quintet	−4.25, quintet	−5.70, double triplet, $J_1 = J_2 = 12$, $J_3 = 6.9$	−4.25, doublet, $J = 6.9$	−3.21, doublet, $J = 12$	−1.55, triplet	...	...
1-*p*-Anisyl-π-allylpalladium chloride dimer	−3.38, doublet, $J = 11.6$	−4.24, multiplet	−5.48, multiplet	−4.24, doublet, $J = 7.0$	−3.19, doublet, $J = 11.6$	...	7.17, AB quartet, $J = 8.1$	...
4-Phenyl-π-cyclohexenylpalladium chloride dimer	−3.70, multiplet	−5.63, multiplet	−6.03, triplet	...	−5.63, multiplet	...	−7.64, singlet	−1.55, −2.37, multiplet

[a] Chemical shifts referred to an external hexamethyldisiloxane standard; *J* values are in cycles per seconds. [b] H_B and H_E give overlapping multiplets.

20 ml of butadiene, and 100 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile solution was stirred at room temperature overnight and the product was isolated as in the examples above. The yellow oil obtained after chromatography was crystallized by adding pentane slowly to a methylene chloride solution. Initially a dark oil separated. This was discarded and addition of more pentane produced yellow crystals. Two recrystallizations from methylene chloride and pentane gave 0.25 g (10%) of product. The complex was apparently unstable and further attempts to purify it by rechromatographing or recrystallizing gave a less pure product.

1-Phenyl-π-(2,4)-cyclohexenylpalladium Chloride Dimer. A reaction mixture containing 6.28 g (20 mmol) of phenylmercuric chloride, 20 ml of 1,3-cyclohexadiene, and 200 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile solution was stirred at room temperature overnight. The product was isolated as a yellow oil. Addition of pentane to a methylene chloride solution of the oil gave first a dark oil which was discarded, and then yellow crystals. Two further recrystallizations from methylene chloride by adding pentane gave a 1% yield of a pure product.

1-(2-Phenylethyl)-π-allylpalladium Chloride Dimer. A reaction mixture containing 1.91 g (5 mmol) of dibenzylmercury (Metallomer Laboratories), 15 ml of isoprene, and 100 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile solution was stirred at room temperature overnight. The product was isolated as in the preceding example. There was obtained about a 1% yield of a yellow crystalline product.

1-Benzyl-2-methyl-π-allylpalladium Chloride Dimer Prepared from Tetraphenyltin. A reaction mixture containing 2.13 g (5 mmol) of tetraphenyltin, 5 ml of isoprene, and 50 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile was stirred at room temperature overnight. The product was isolated as in the preparation from phenylmercuric chloride. There was obtained 0.27 g (19.5%) of yellow crystalline product.

Anal. Calcd for $C_{22}H_{26}Cl_2Pd_2$: C, 46.02; H, 4.56. Found: C, 45.23; H, 4.63.

1-Phenyl-3-buten-2-yl Acetate. In each of three heavy-walled Pyrex bottles was placed 16.80 g (50 mmol) of phenylmercuric acetate, 0.11 g (0.5 mmol) of palladium acetate, and 24.35 g (55 mmol) of lead tetraacetate. The bottles were capped with butyl rubber lined metal caps and 50 ml of acetonitrile and 10 ml of butadiene were injected by hypodermic syringe, puncturing the rubber liner, through a small hole in the metal cap. The mixtures were stirred at room temperature overnight. Analyses by glpc (6-ft Carbowax 20M column) showed the solutions to be 0.78 *M* in 1-phenyl-3-buten-2-yl acetate. The product in the combined reaction mixture was isolated by pouring them into water and extracting with five portions of pentane. The extracts were washed with water and aqueous sodium bicarbonate and then dried over anhydrous magnesium sulfate. Distillation of the extract gave 9.6 g of colorless liquids, bp 87–91° (2 mm), and 4.6 g of bp 110–140° (2 mm). The first fraction was about 90% 1-phenyl-3-buten-2-yl acetate and the second fraction about 25% the same product. A pure sample, isolated by preparative glpc gave the expected analyses and nmr spectrum for 1-phenyl-3-buten-2-yl acetate.

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 74.88; H, 7.58.

The nmr spectrum had bands at about −7.38 (singlet, five protons), −2.00 (singlet, three protons), −3.00 (doublet, two-protons), and −5.00 to −6.00 ppm (multiplet, four protons) assuming the CH_3COO– protons are at −2.00 ppm.

1-*p*-Anisyl-3-buten-2-yl Acetate and 1-*p*-Anisyl-2-buten-4-yl Acetate. Each of three heavy-walled bottles was charged with 8.86 g (20 mmol) of lead tetraacetate and 7.32 g (20 mmol) of *p*-anisylmercuric chloride. The bottles were capped as in the previous experiment and 6 ml of butadiene and 20 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile solutions were injected into each. After stirring at room temperature overnight, the reaction mixtures were combined and the products isolated as in the preceding experiment. There was obtained 2.32 g of product, bp ~130° (2 mm), which, by glpc, was found to be about 80% of a 3:1 mixture of 1-*p*-anisyl-3-buten-2-yl acetate and 1-*p*-anisyl-2-buten-4-yl acetate, respectively. Samples of each were isolated by preparative glpc and identification was made on the basis of their nmr spectra.

The nmr spectrum of the major product had bands at −7.00 (AB quartet, four protons), −3.80 (singlet, three protons), −2.00 (singlet, three protons), −2.90 (doublet, two protons), and at −4.50 to −5.20 ppm (multiplets, four protons) assuming the CH_3COO– protons are at −2.00 ppm. The minor product in the mixture had nmr bands at −6.90 (AB quartet, four protons), −3.80 (singlet, three protons), −2.0 (singlet, three protons), −3.30 (doublet, two protons), −4.50 (doublet, two protons), and at −5.69 ppm (multiplet, two protons) assuming the CH_3COO– protons are at −2.00 ppm.

β-Phenethyl Acetate. A heavy-walled Pyrex bottle containing 3.36 g (10 mmol) of phenylmercuric acetate and 8.8 g (20 mmol) of lead tetraacetate was capped as in previous experiments and flushed with ethylene. After injecting 10 ml of acetonitrile the bottle was pressured to 50 psi with ethylene and 1 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile was injected. After stirring at room temperature overnight, glpc analyses showed the solution to be 0.155 *M* in β-phenethyl acetate and 0.190 *M* in styrene.

1-Phenyl-2-propyl Acetate. A reaction was carried out as in the preceding example with 3.36 g (10 mmol) of phenylmercuric ace-

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(9) O. Dimroth, *Chem. Ber.*, 35, 2867 (1902).

tate, 4.87 g (11 mmol) of lead tetraacetate, 0.022 g (0.1 mmol) of palladium acetate, and 10 ml of acetonitrile under 40 psi of propylene at 50° for 2 hr. Analyses of glpc showed that the solution was now 0.141 *M* in 1-phenyl-2-propyl acetate and 0.09 *M* in *trans*-1-phenyl-1-propene.

Acknowledgments. The nmr spectra were measured by Mr. C. R. Boss and Dr. M. M. Anderson. The experimental work was carried out with the assistance of Mr. Joseph Keelins.

A Synthesis of Diaryl Ketones from Arylmercuric Salts

R. F. Heck

Contribution from the Research Center of Hercules Inc.,
Wilmington, Delaware 19899. *Received December 7, 1967*

Abstract: Arylmercuric chlorides react with carbon monoxide and palladium or rhodium halide catalysts to form diaryl ketones in fair yields.

Chlorobis(triethylphosphine)methylpalladium reacts readily with carbon monoxide to form the corresponding acylpalladium compound.[1] Carbon monoxide insertions also appear to occur in numerous palladium-catalyzed carbonylation reactions. For example, in the formation of esters from olefins[2] or dienes,[3] in the formation of 3-chloroacyl chlorides from olefins,[4] in the formation of muconic acid esters from acetylene,[5] in the carbonylation of allylic halides,[6] or π-allylpalladium halides,[7] and in the synthesis of isocyanates from amines and carbon monoxide.[8,9] Recently Henry[9] has found that arylpalladium salts, prepared *in situ* from arylmercuric salts and various palladium compounds, react with carbon monoxide in hydroxylic solvents to form arylcarboxylic acids or their derivatives depending upon the solvent. While investigating this reaction independently, it was found that under some conditions diaryl ketones could also be formed in moderate yields from arylmercuric salts and carbon monoxide with a palladium salt catalyst. Rhodium trichloride and its trialkylphosphine derivatives proved to be better catalysts than palladium salts; they produced diaryl ketones in better yields, generally without the concurrent formation of appreciable amounts of carboxylic acid derivatives.

Results and Discussion

The diaryl ketones were generally prepared by combining an arylmercuric salt or other arylating agent and the catalyst in a solvent, such as acetonitrile under about 50 psig of carbon monoxide with stirring for 1–24 hr at 25–100° depending upon the reactants. The experiments are summarized in Table I.

Arylmercuric chlorides react with palladium salts in the absence of carbon monoxide to form biaryls in good yields.[10] The addition of carbon monoxide to the reaction mixture results in the formation of benzoyl chlorides or benzoate esters and diaryl ketones at the expense of the biaryls. At 50 psig of carbon monoxide generally little biaryl is formed. Diaryl ketones appear to be formed in preference to benzoyl chlorides or benzoate esters at higher pressures of CO. The use of rhodium catalysts for the diaryl ketone syntheses is preferred because generally much less of the biaryl and benzoic acid derivatives are formed relative to the diaryl ketone, and because mercuric chloride is apparently able to reoxidize Rh(I) to the catalytically active Rh(III). To achieve a catalytic reaction with palladium, stoichiometric amounts of cupric chloride are required.

Diaryl ketones are produced by this reaction in a variety of solvents, but hydroxylic solvents are generally to be avoided because larger amounts of benzoic acid derivatives are usually formed in these solvents. Acetonitrile has proved to be the most useful solvent. Acetone may also be used. Even hydrocarbons such as toluene can be used if toluene soluble catalysts of the type $RhCl(CO)(PR_3)_2$ are employed.

The mechanism of formation of diaryl ketones from arylmercuric chlorides is not clear, but probably it involves a reaction of an acylpalladium (or rhodium) compound with an arylpalladium (or rhodium) or arylmercuric compound. Aroyl chlorides and biaryls are probably formed by the side reactions

$$\mathrm{ArHgCl} + \mathrm{PdCl_2} \rightleftharpoons (\mathrm{ArPdCl}) + \mathrm{HgCl_2}$$

$$(\mathrm{ArPdCl}) + \mathrm{CO} \rightleftharpoons (\mathrm{ArCOPdCl})$$

$$(\mathrm{ArCOPdCl}) + (\mathrm{ArPdCl}) \longrightarrow \mathrm{ArCOAr} + \mathrm{PdCl_2} + \mathrm{Pd}$$

or

$$(\mathrm{ArCOPdCl}) + \mathrm{ArHgCl} \longrightarrow \mathrm{ArCOAr} + \mathrm{HgCl_2} + \mathrm{Pd}$$

$$2(\mathrm{ArPdCl}) \longrightarrow \mathrm{Ar{-}Ar} + \mathrm{PdCl_2} + \mathrm{Pd}$$

$$(\mathrm{ArPdCl}) + \mathrm{ArHgCl} \longrightarrow \mathrm{Ar{-}Ar} + \mathrm{HgCl_2} + \mathrm{Pd}$$

$$(\mathrm{ArCOPdCl}) \longrightarrow \mathrm{ArCOCl} + \mathrm{Pd}$$

We have not observed the formation of benzil-type products by coupling of two acylpalladium (rhodium) compounds even at very high carbon monoxide pres-

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