October, 1977] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (10), 2741—2743 (1977) 2741

RhCl(PPh3)3-catalyzed Coupling of Diorganomercurials

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(Received March 11, 1977)

$RhCl(PPh_3)_3$ has been proved to be an effective catalyst for the reaction of various diorganomercurials to give such coupling products as conjugated diyne, conjugated diene, biaryl, and alkane in good yields under mild conditions. A probable mechanism including the oxidative addition of organomercurials to a rhodium complex and the subsequent reaction of two oxidative-addition adducts to yield the product was presented.

Organomercurials are attractive substrates for organic syntheses,[1] since pure substances, including configurationally pure ones,[2] are easily obtainable. In our previous study of the palladium(0)-catalyzed reaction of organomercurials with acyl halides, the coupling product of organomercurial (R–R) was obtained in a rather large quantity, accompanied by the desired ketone:[3]

$$R_2Hg + R'COBr \xrightarrow{Pd(PPh_3)_4} RCOR' + \underset{\text{(minor product)}}{R\text{–}R}$$

As for the decomposition of organomercurials, it is well known that it occurs only at elevated temperatures (generally above 300 °C). In the presence of some transition-metal compounds (Pt, Pd, Ag) the required temperature for the decomposition was lowered, but the conditions were still very drastic.[4] We examined the reaction in detail for the purpose of obtaining the coupling product under mild conditions and found that tris(triphenylphosphine)chlororhodium ($RhCl(PPh_3)_3$) is particularly effective for the reaction. While we have been continuing our study, several papers concerning the palladium-assisted coupling of organomercurials have appeared.[5] Here in this paper we will report the rhodium-catalyzed coupling of organomercurials, which is a more convenient system for the reaction.[6]

Results and Discussion

Reaction Conditions. The decomposition of diphenylmercury was examined with various catalysts and solvents; the results are compared in Table 1. The control experiment showed that a catalyst was essential for the reaction under the conditions examined. The decomposition of $Pd(PPh_3)_4$ occurred, and the reaction was incomplete (Run 1). $RuCl_2(PPh_3)_3$ showed little activity (Run 4). Contrary to palladium or ruthenium complex, $RhCl(PPh_3)_3$ was very effective as a catalyst and biphenyl was obtained quantitatively (Run 5 and Table 2). This implies that two phenyls in diphenylmercury are available for the reaction. Mercury metal was also separated quantitatively. Thus, the stoichiometry of rhodium-catalyzed coupling can be represented by the following equation:

$$(C_6H_5)_2Hg \xrightarrow{RhCl(PPh_3)_3} (C_6H_5)_2 + Hg$$

TABLE 1. CATALYTIC COUPLING OF Ph_2Hg[a]

Run	Catalyst	Solvent	Time h	Biphenyl[b] %
1	$Pd(PPh_3)_4$	HMPA	4	13
2	$Pd(PPh_3)_4$	CH_3CN	8	31
3	$Pd(PPh_3)_4$	THF	8	16
4	$RuCl_2(PPh_3)_4$	HMPA	4	1
5	$RhCl(PPh_3)_3$	HMPA	4	100
6	$RhCl(PPh_3)_3$	CH_3CN	4	96
7	$RhCl(PPh_3)_3$	DMF	15	36
8	$RhCl(PPh_3)_3$	DMSO	4	20
9	$RhCl(PPh_3)_3$	toluene	4	13
10	$RhCl(PPh_3)_3$	THF	4	4
11[c]	$RhCl(PPh_3)_3$	HMPA	4	49
12[d]	$RhCl(PPh_3)_3$	HMPA	4	10
13[e]	$RhCl(PPh_3)_3$	HMPA	1	8

a) Catalyst; 0.0065 mmol, Ph_2Hg; 0.25 mmol, solvent; 2 ml, temp.; 80 °C, under N_2. b) GLC analysis using an internal standard. c) PPh_3; 0.065 mmol. d) Under air. e) Galvinoxyl; 0.04 mmol.

Amoung the solvents examined, HMPA and acetonitrile gave better results. The reaction was pronouncedly retarded with galvinoxyl or oxygen. Inhibition by excess triphenylphosphine was also observed.

Syntheses of Conjugated Diynes, Conjugated Dienes, Biaryls, and Alkanes. Rhodium-catalyzed coupling was applied to the syntheses of various hydrocarbons. The results are listed in Table 2. In all cases, pure products were isolated with simple treatments. Thus, this catalytic reaction may be valuable for the syntheses of symmetrical conjugated diyne, symmetrical conjugated diene, and biaryl. The case of dibutylmercury was exceptional; the coupling product, octane, was never detected, as is shown in Run 25, although dibutylmercury undoubtedly reacted with the rhodium catalyst, even at room temperature. The red color of the catalyst

TABLE 2. $RhCl(PPh_3)_3$-CATALYZED SYNTHESIS OF DIYNE, DIENE, BIARYL, AND ALKANE

Run	R_2Hg R	Temp °C	Time h	R_2Hg/Rh mol ratio	R–R %
21	$PhC{\equiv}C$	50	1	200	95
22	(E)-$PhCH{=}CH$	70	1	50	99[a]
23	p-CH_3-C_6H_4	80	4	30	86
24	p-Cl-C_6H_4	80	4	30	91
25	Bu	130	4	30	0[b]
26	$PhCH_2$	130	8	30	44[b]

a) (E,E). b) GLC analysis using an internal standard.

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immediately changed into black when dibutylmercury was added. Presumably some side reaction, *e.g.* β-elimination of hydrorhodium in the organorhodium intermediate, would occur preferentially. Dibenzylmercury afforded 1,2-diphenylethane only on being heated to an elevated temperature.

Reaction Mechanism. The initial stage of the reaction is probably an oxidative addition of organomercurials to the rhodium catalyst:

$$R_2Hg + RhCl(PPh_3)_2 \longrightarrow \underset{\mathbf{1}}{(R)(RHg)RhCl(PPh_3)_2} \quad (1)$$

There are examples of the oxidative addition of organomercurials to such transition-metal complexes as Pd, Rh, Ir, and Pt.[7] The present result of the supression of the catalytic reaction by the addition of triphenylphosphine supports the idea.[8]

The coupling products are expected to be produced by the reaction of the oxidative-addition adduct(s). There is evidence that the reaction is not such a simple unimolecular demercuration as is shown in Eq. 2, which was suggested by Birch *et al.* for the reaction of Ref. 5a:[9]

$$R_2Hg + Rh \longrightarrow \underset{\mathbf{1}}{R\text{-}Rh\text{-}HgR} \xrightarrow{-Hg} R\text{-}Rh\text{-}R \longrightarrow R\text{-}R + Rh \quad (2)$$

A competitive reaction of an equimolar mixture of diphenylmercury and bis(p-tolyl)mercury afforded biphenyl, 4-methylbiphenyl, and 4,4′-dimethylbiphenyl (Table 3). The statistical ratio in diaryls indicates that the catalytic reaction does not follow Eq. 2; if it did, the molar ratio of Ph–Ph: Ph–Tol: Tol–Tol should be 1: 0: 1. Here, it should be noticed that the redistribution between diphenylmercury and bis(p-tolyl)mercury does not take place rapidly.[10]

TABLE 3. COMPETITIVE REACTION OF Ph_2Hg AND $(p\text{-Tol})_2Hg$[a)]

$$Ph_2Hg + (p\text{-Tol})_2Hg \xrightarrow[Rh]{} Ph-Ph + Ph-Tol\text{-}p + p\text{-Tol}-Tol\text{-}p$$

Conversion[b)] %	Relative mol ratio		
	Ph−Ph	Ph−Tol-p	p-Tol−Tol-p
8	1.3	2.0	0.9
30	1.3	2.0	0.8
90	1.1	2.0	1.0

a) Ph_2Hg; 0.1 mmol, $(p\text{-Tol})_2Hg$: 0.1 mmol, RhCl-$(PPh_3)_3$; 0.0065 mmol, HMPA; 2 ml, 80 °C, under N_2. b) Converison based on Ph_2Hg consumed.

At the present time, we propose the next reaction as the most plausible mechanism for the reductive elimination; in this reaction two molecules of **1** yield a coupling product:

$$\underset{\mathbf{1}}{2(R)(RHg)RhCl(PPh_3)_2} \longrightarrow R\text{-}R + 2RhCl(PPh_3)_2 + R_2Hg + Hg \quad (3)$$

Similar "complex" bimolecular reactions yielding organic coupling products are frequently found in organo-transition metal chemistry.[12]

Experimental

Materials. Commercial diphenylmercury and galvinoxyl were used without further purification. The $RhCl(PPh_3)_3$,[13] $RuCl_2(PPh_3)_3$,[14] $Pd(PPh_3)_4$,[15] and bis(2-phenylethynyl)mercury[16] were prepared by previously reported methods. The other organomercurial was prepared from a Grignard reagent and $HgCl_2$ according to a procedure in the literature[17] and was distilled or recrystallized from ethanol or benzene. The solvents were dried over a molecular sieve (3A).

Procedure. *Preparation of Biphenyl*: In a typical run (Run 5), a solution of diphenylmercury (89 mg, 0.25 mmol), $RhCl(PPh_3)_3$ (6 mg, 0.0065 mmol), and HMPA (2 ml) was stirred at 80 °C for 4 h under nitrogen. After the mercury metal had then been separated by decantation, aqueous sodium chloride (5 ml, 12.5%) was added to the resulting solution, and the organic materials, extracted with 4 ml of ether, were washed with 5 ml of 12.5% aqueous sodium chloride. Then the ether layer was treated with an ether solution of iodine to decompose the unreacted diphenylmercury. Subsequent analysis by GLC (Hitachi Perkin-Elmer F6D, 35% silicon DC 200 on Celite 545, 1 m, 170 °C, 0.5 kg cm^{-2} of N_2) revealed 38.6 mg (0.25 mmol) of biphenyl and a trace amount of iodobenzene. The separated mercury metal, after it had been washed several times with acetone and air-dried, weighed 48.2 mg (0.24 mmol).

Preparation of 1,4-Diphenyl-1,3-butadiyne: A mixture of bis(2-phenylethynyl)mercury (503.5 mg, 1.25 mmol), RhCl $(PPh_3)_3$ (6 mg, 0.0065 mmol), and HMPA (3 ml) was stirred at 50 °C for 1 h under nitrogen. Aqueous sodium chloride (10 ml. 12.5%) was then added to the mixture, and the organic materials were extracted with 10 ml of ether. The aqueous layer was extracted two times with 5-ml portions of ether. After the ether extract had been washed with two 5-ml portions of 12.5% aqueous sodium chloride, the ether was removed under reduced pressure. The purification of the residual solid by column chromatography on silica gel (2 g), using hexane as the eluant, gave 239 mg of 1,4-diphenyl-1,3-butadiyne (94.5%). Mp 86—86.5 °C (lit,[18] 87—88 °C) Found: C 95.13; H, 4.90%. Calcd for $C_{16}H_{10}$: C, 95.01; H, 4.99%.

*Preparation of (*E,E*)-1,4-Diphenyl-1,3-butadiene*: A mixture of bis((E)-2-phenylethenyl)mercury (101.7 mg, 0.25 mmol), $RhCl(PPh_3)_3$ (4.6 mg, 0.005 mmol), and HMPA (1 ml) was stirred at 70 °C for 1 h under nitrogen. Treatment similar to that described above gave 50.4 mg of (E,E)-1,4-diphenylbutadiene (99%). Mp 153.5—154 °C (lit,[19] 153—153.5 °C) Found: C, 93.16; H, 6.86%. Calcd for $C_{16}H_{14}$: C, 93.15; H, 6.85%.

Preparation of 4,4′-Dimethylbiphenyl: A mixture of bis(p-tolyl)mercury (574.8 mg, 1.50 mmol), RhCl $(PPh_3)_3$ (46.3 mg, 0.050 mmol), and HMPA (5 ml) was stirred at 80 °C for 4 h under nitrogen. Treatment similar to that above gave 234 mg of 4,4′-dimethylbiphenyl (86%). Mp 121.5 °C (lit,[20] 122 °C). Found: C, 91.97; H 7.86%. Calcd for $C_{14}H_{14}$: C, 92.24; H, 7.76%.

Preparation of 4,4′-Dichlorobiphenyl: A mixture of bis(p-chlorophenyl)mercury (635.4 mg, 1.50 mmol), $RhCl(PPh_3)_3$ (46.0 mg, 0.050 mmol), and HMPA (5 ml) was stirred at 80 °C for 5 h under nitrogen. Treatment similar to that above gave 304 mg of 4,4′-dichlorobiphenyl (91%). Mp 147—147.5 °C (lit,[21] 147—148 °C). Found: C, 64.55; H, 3.63%. Calcd for $C_{12}H_8Cl_2$: C, 64.60; H, 3.62%.

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