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FORMATION OF DIARYLS BY THERMAL DECOMPOSITION OF RHODIUM(I) TRIARYLPHOSPHINE COMPLEXES

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Summary

Chlorotris(triphenylphosphine)rhodium, $RhCl(PPh_3)_3$ undergoes thermal decomposition above 140°C in solution and in the solid state to yield biphenyl. Rhodium complexes with *para*-substituted triphenylphosphine ligands form exclusively 4,4′-disubstituted biphenyls. Mixtures of two complexes $RhCl(PAr_3)_3$ and $RhCl(PAr'_3)_3$ form the crossed diaryl ArAr′ and two non-crossed compounds $(Ar)_2$ and $(Ar')_2$. The mechanism is assumed to involve dissociation of $RhCl(PPh_3)_3$ into PPh_3 and solvated $RhCl(PPh_3)_2$ followed by oxidative addition of the liberated phosphine to the latter bis-triphenylphosphine compound. Evidence for a phenyl-rhodium intermediate has been provided by phenylation of styrene by $RhCl(PPh_3)_3$. In an independent process, $RhCl(PPh_3)_3$ forms benzene by an *ortho*-metallation route.

Introduction

Chlorotris(triphenylphosphine)rhodium, $RhCl(PPh_3)_3$, (I) was independently synthesized by three groups in 1965 [1—3] and was later shown to be a most versatile homogeneous metal catalyst for organic reactions. The applications of the complex and mechanistic details of its reactions had been discussed in over five hundred publications, but studies of transformations of the ligands at elevated temperatures have received little attention. It has been implied that various hydrogen donors are capable of inducing reversible elimination of the chlorine atom as HCl [4]. There is controversy about the mode of dissociation and dimerization of I to give free PPh_3 and mono- or dimeric bis(triphenylphosphine)rhodium complex [5—10]. The phosphine ligands which remain attached to the metal atom are claimed to undergo aerial oxidation to give coordinated triphenylphosphine oxide [11] and to form benzene and biphenyl in the presence of potent hydrogen donor reagents [12].

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We now report a reaction of I, overlooked in previous studies, in which carbon—phosphorus bonds are cleaved to give biphenyl.

Results

On reinvestigation of some $RhCl(PPh_3)_3$-catalyzed decarbonylation reactions of aromatic aldehydes [13,14] we observed that substantial quantities of biphenyl accompanied the expected products. The yields of biphenyl proved to depend on the amount of catalyst employed. Since biphenyl was formed also by heating of the rhodium complex at 170—180°C in aldehyde-free solvents (benzene, toluene, xylenes, mesitylene, 1-methylnaphthalene, diphenyl ether) or even upon thermolysis of the solid $RhCl(PPh_3)_3$ (both allotropic forms [15]), we concluded that the origin of the biphenyl is the triphenylphosphine ligands rather than the aldehydic reagent.

Typically, 14 mol % of biphenyl was obtained when 50 mg of I * was heated in 1.5 cm^3 of toluene at 180°C (sealed tube) for 5 h. The formation of biphenyl can be speeded up by increasing the temperature. However, owing to side reactions (vide infra) the rate-temperature dependence does not obey the Arrhenius law. It is noteworthy that biphenyl is formed even below the m.p. of solid I (i.e. below 157—158°C [5]), and therefore its production cannot be regarded as due merely to pyrolytic decomposition. E.g., a toluene solution of 3×10^{-2} *M* of I gives 3.5 mol % of biphenyl after 3 h at 140°C.

In all the above experiments (including decomposition of solid I) varying amounts of benzene were formed along with the biphenyl. However, while the formation of C_6H_6 depends on the ability of the medium to function as a hydrogen donor, the process leading to biphenyl is less affected by the nature of the solvent. The solvent is of importance, however, in connection with the atmosphere above the reaction mixture. In alkylbenzene solvents biphenyl formation takes place equally well under nitrogen and under ambient atmosphere. In benzene a small amount of air is required to ensure the transformation of I at a measurable rate (cf. the activation of I in catalytic isomerization and hydrogenation reactions [16,17]).

Addition of free triphenylphosphine to the reaction mixture inhibits the process to a certain extent. Likewise the rate is decreased by an excess of O_2, H_2O, MeOH or hydrogen halide. An experiment conducted for 3 h with 5.4×10^{-5} and 9.5×10^{-5} mol of PPh_3 led to reductions of 60 and 90% respectively, in biphenyl formation, as compared with that in absence of added phosphine. Addition of larger quantities of PPh_3 (i.e. >1.8 mol per mol of I) does not cause further decrease in the yield of the biphenyl.

The bromo- and iodo-analogs of $RhCl(PPh_3)_3$ (I), bromotris(triphenylphosphine)rhodium $RhBr(PPh_3)_3$, (II) [5] and iodotris(triphenylphosphine)rhodium $RhI(PPh_3)_3$ (III) [5] also decompose at elevated temperatures to give biphenyl, albeit at lower rates. Biphenyl formation from I follows pseudo zero order kinetics for the first 4 h at a rate of 9.7×10^{-4} mol % s^{-1} (180°C, 5×10^{-2} *M* in toluene). Under the same conditions a rate of 5.0×10^{-4} % s^{-1} was observed for the first 3 h when the iodo complex III was used. The rate for the bromo-

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* Commercial samples purchased from Stream Chemical Incorp. Freshly prepared samples of I, free from any triphenylphosphine oxide, yielded up to 54 mol% of biphenyl under similar conditions.

compound II was found to be intermediate for times less than 30 min but subsequently side reactions, including elimination of elementary bromine, seem to prevail and the formation of biphenyl starts to fall off.

When chlorotris(triarylphosphine)rhodium complexes of general formula $RhCl[(4\text{-}XC_6H_4)_3P]_3$ were decomposed in toluene at 180°C the compounds in which X = CH_3O, CH_3, F and Cl (IV—VII) yielded exclusively 4,4'-disubstituted biphenyls free of any other isomeric diaryls.

Under comparable conditions, the initial rates of diaryl formation from $RhCl(PPh_3)_3$ (I), $RhCl[(4\text{-}CH_3C_6H_4)_3P]_3$ (V), $RhCl(4\text{-}FC_6H_4)_3)]_3$ (VI) and $RhCl(4\text{-}ClC_6H_4)_3P]_3$ (VII) were 6.5, 2.7, 2.3 and 0.4×10^{-4} mol % s^{-1}, respectively. This suggests that electron donating groups promote the process while electron attracting substituents slow it down. The somewhat low activity of the *p*-tolylphosphine complex V may be attributed either to enhanced formation of toluene in a side reaction or to the fact that this complex could not be obtained analytically pure by any of the reported methods [9,18] (see Experimental).

The recorded rate of 4,4'-dianisyl formation from $RhCl[(4\text{-}CH_3OC_6H_4)_3P]_3$ IV was similar to that for the transformation product of VI. This can be explained by assuming interaction of the methoxy group with the metal atom, as reported for some other reactions of transition metal complexes [19].

Mixtures of two rhodium complexes $RhCl(PAr_3)_3$ having different Ar groups give "mixed" and "non-mixed" diaryls. E.g., equimolar quantities of $RhCl(PPh_3)_3$ (I) and $RhCl[(4\text{-}CH_3C_6H_4)_3P]_3$ (V) yield (at 190°C) biphenyl, 4-methylbiphenyl and 4,4'-bitolyl in a ratio of 1 : 2 : 1. Owing to ligand exchange these diaryls are also obtained when I is heated in the presence of (excess) free tri-*p*-tolylphosphine or by treatment of V with PPh_3. A mixture of biphenyl, 4-methylbiphenyl and 4,4'-bitolyl in ratio 4 : 4 : ~1 is formed also when $RhCl[(C_6H_5)_2(4\text{-}CH_3C_6H_4)P]_3$ (VIII) is decomposed in toluene at 190°C.

Discussion

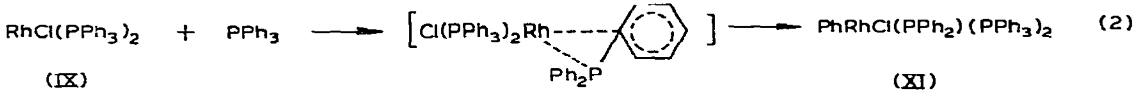
Triarylphosphine ligands of some transition metal complexes have been shown to undergo carbon—phosphorus bond cleavage, to give transferable aryl groups [20—22], and frequently diaryl formation [12,20—28]. Oxidative addition of PAr_3 [22], *ortho*-metallation [29], free radical and benzyne intermediacy [26] have been considered as key steps in the transformation of the complexes into diaryls. It seems, in fact, that the various phosphine complexes decompose in different ways.

Having shown that complexes $RhCl[(4\text{-}XC_6H_4)_3P]_3$ give exclusively 4,4'-disubstituted diaryls, we can rule out both *ortho*-metallation and benzyne intermediacy. These results also disfavor a free radical mechanism, although the necessity of oxygen for the decomposition of I in benzene solution might have suggested free radical involvement. Unambiguous evidence for a non-radical mechanism has been provided by two experiments in which either a free radical scavenger (0.1 mol of 2,5-di-tert-butylhydroquinone per mol of I), or free radical initiator (0.1 mol α,α-azobisisobutyronitrile per mol of I) was added. In both cases the rate of biphenyl formation was the same and identical with that of the additive-free control reaction. We thus assume that $RhCl(PPh_3)_3$ (I) gives biphenyl via oxidative addition. Such a mechanism is in agreement with the general trend in the observed electronic effect.

Free PPh_3 is formed both by dissociation and by dimerization of I. These processes have recently been shown [10] to take place as two consecutive equilibria (eq. 1):

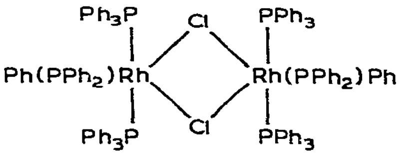
$$\underset{(I)}{2\,RhCl(PPh_3)_3} \rightleftharpoons \underset{(IX)}{RhCl(PPh_3)_2} + \underset{(I)}{RhCl(PPh_3)_3} + PPh_3 \rightleftharpoons \underset{(X)}{[RhCl(PPh_3)_2]_2} + 2\,PPh_3 \qquad (1)$$

By analogy with the reaction of triphenylphosphine with some zero valent nickel and palladium complexes, the liberated PPh_3 is assumed to add to IX to yield a phenyl-rhodium compound IX via a concerted three centered process (eq. 2).



The possibility that XI results from an intramolecular insertion reaction into I rather than by addition of free phosphine to IX can be excluded both by virtue of the inhibition effect of PPh_3, discussed below, and by the fact that mixed biphenyls are obtained from mixtures of arylphosphine complexes.

Complex XI is likely to be stabilized as Cl- or Ph_2P-bridged dimers [20] [E.g.,



(XII)

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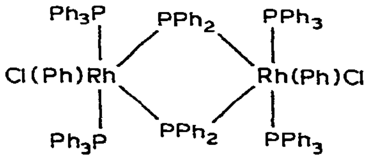

(XIII)

Although no phenyl-rhodium complex was isolated from a heated solution of I, its participation was confirmed by an experiment in which styrene was used as solvent. Upon brief heating of the solution (10 min) small amounts of 1,1-diphenylethylene and *trans*-stilbene were formed along with the biphenyl. (Cf. e.g., the phenylation of styrene by phenyl-palladium complexes generated from palladium acetate and various phenyl-donating reagents [30]).

Phenyl-rhodium(I) compounds have been shown to react with phenylating agents to give biphenyl [31]. In this case, as in analogous arylations (see ref. 20, a bis(phenyl)-metal intermediate is assumed to be formed and to undergo reductive elimination in the final step. As IX is already a five coordinated Rh^{III} compound, and ESR measurements indicate that neither Rh^{II} nor Rh^{IV} species are present, we must conclude that either elimination of Ph_2PCl from IX or an intramolecular reaction takes place.

The moderate influence of added PPh_3 on the biphenyl formation can be rationalized in terms of two opposing effects. On the one hand the phosphine promotes the reaction as an essential reagent, but on the other hand it shifts the equilibrium $I \rightleftharpoons IX + PPh_3$ to the left, and subsequently lowers the concentration of the reacting bis-triphenylphosphine complex IX. It is understandable that some reagents other than tertiary phosphine (e.g. HCl, H_2O, MeOH and excess O_2) compete with PPh_3 in the oxidative addition process, and so strongly inhibit the conversion of I into biphenyl.

In contrast to some palladium-phosphine complexes [26], benzene is formed in the thermal decomposition of I even in the absence of an external hydrogen donor. The ratio of biphenyl : benzene ranges from 0.3 to 2.0 under our experimental conditions. This implies that *ortho*-metallation is a significant feature of $RhCl(PPh_3)_3$ (I). It should be recalled that the iridium analogue of I, $IrCl(PPh_3)_3$ (XIV) has been reported [32] to exist in solution entirely as the hydride $HIr[(o\text{-}C_6H_4)PPh_2](PPh_3)_2$ (XV) [^{1}H NMR (C_6H_6) δ −18.7 ppm]. We have now shown that I also exists to some extent as $HRhCl[(o\text{-}C_6H_4)PPh_2](PPh_3)_2$ (XVI). The FT ^{1}H NMR of I in $CDCl_3$ shows after 2500 scannings at 140°C, a differnetiated multiplet centered at δ —16.1 ppm (width 2.0 ppm). We conclude that, in contrast to the transformation of I into biphenyl, the formation of benzene is associated with this internal hydride transfer. Obviously, an external hydrogen donor (e.g., indoline or pyrrolidine) promotes the formation of benzene, as already noted [12].

Experimental

$RhCl(PPh_3)_3$ (I) [33], $RhBr(PPh_3)_3$ (II) [5], $RhI(PPh_3)_3$ (III) [35] and $RhCl[(4\text{-}FC_6H_4)_3P]_3$ (VI) [34] were prepared as described in the literature. Numerous attempts to synthesize chlorotris(tri-4-tolylphosphine)rhodium (V) from $[(C_2H_4)_2RhCl]_2$ according to Tolman et al. [9] led to preparations of samples with a somewhat low carbon content just as reported for the alternative synthesis from PPh_3 and $[(1,5\text{-}C_8H_{12})RhCl]_2$ [18]. Therefore, we used solutions of V prepared in situ by heating a mixture of 150 mg of $[(C_2H_4)_2RhCl]_2$, 425 mg of PPh_3 and 15 cm^3 of toluene under Ar at 50°C until evaporation of ethylene ceased. The same method was applied also for the preparation of $RhCl[(4\text{-}CH_3OC_6H_4)_3P]_3$ (IV) and of $RhCl[(C_6H_5)_2(4\text{-}CH_3C_6H_4)P]_3$ (VIII).

Chlorotris(tri-4-chlorophenylphosphine)rhodium, $RhCl[(4\text{-}ClC_6H_4)_2P]_3$ (VII).

A hot solution of 1.75 g of tri-4-chlorophenylphosphine in 50 cm^3 ethanol was added to a solution of 0.25 g of $RhCl_3$, 3 H_2O in the same solvent. The mixture was stirred and refluxed under N_2 for 30 min to yield 996 mg (85%) of orange crystals. These were analytically pure after washing with cold ethanol. M.p. 164°C. Found: C, 52.2; H, 2.9; Cl, 28.7. $C_{54}H_{36}Cl_{10}P_3Rh$. Calcd.: C, 52.5; H, 3.0; Cl, 28.7%.

Previously, VII has been prepared only in situ without isolation.

Thermal decomposition of the rhodium complexes

The transformation of the various complexes is illustrated by the following example:

A 3 cm^3 pressure tube (wall thickness 3 mm) was carefully dried and charged with a solution of 50 mg of $RhCl(PPh_3)_3$ (I), in 1.5 cm^3 of hot benzene (AR grade). The tube was sealed under 1 atm dry air at 25°C and immersed (bulb and neck) into a preheated oil bath thermostat at 180°C. After 3 h the mixture was cooled, and subjected to preparative TLC on half a glass plate coated with 2 mm of Merck silica 60F. n-Hexane served as eluent. On the second half of the plate a standard solution of biphenyl in benzene (1 mg/cm^3) was run for comparison. The hydrocarbon band was extracted with n-pentane and the concentrated solution analyzed by GLC (Packard 4700 - FID instrument) on a 3000 × 3.175 mm stainless steel column packed with 10% OV-101 on Chromasorb W. In a typical run the yield of biphenyl was 11.4%.

Experiments conducted in high boiling solvents (mesitylene, 1-methylnaphthalene, diphenyl ether) were also performed in open systems, but lack of reproducibility was noted owing to loss of biphenyl by sublimation.

In reactions carried out under an atmosphere other than air, the solvents were degassed and the ampoules were evacuated prior to refilling with the desired gas.

Complexes II—VIII were brought into reaction under similar conditions. Analyses of the products and their comparison with authentic samples of substituted biphenyl prepared previously [36] were carried out on a 3000 × 3.175 mm GLC column packed with 10% Apiezon L on Chromosorb P.

Kinetic measurements were performed using a series of identical reaction tubes charged with equal quantities of the same solution of the complex. The ampoules were all placed in the thermostat at the same time and one tube was withdrawn every 30—60 min and immediately frozen to await GLC analysis.

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