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REACTIONS OF METHYLTRIS(TRIARYLPHOSPHINE)COBALT

I. FORMATION OF BIARYLS

MICHAEL MICHMAN *, VERED R. KAUFMAN and SOPHIA NUSSBAUM

Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem (Israel)

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Summary

Methyltris(triarylphosphine)cobalt $(Ar_3P)_3CoCH_3$, decomposes in solutions of THF, benzene or chlorobenzene to yield biaryls. Coupling to biaryls occurs at the ring carbon originally bonded to phosphorus. Mixed biaryls are obtained from crossover reactions of complexes bearing different triarylphosphine ligands and reactions of complexes with free triarylphosphines.

Introduction

Triarylphosphines and related compounds are commonly regarded as stable and stabilizing ligands in many organometallic compounds. They are used as non-reactive ligands in homogeneous catalysts [1]. They have been used to stabilize alkyl-transition metal compounds of the type used in this work and early examples [2] have been followed by many others [3]. It is therefore important to draw attention to chemical transformations of triarylphosphines in complexes in which the ligand structure is severed. Of these, *ortho*-metallation has been extensively reviewed [4] but few other transformations have been reported. The latter include reactions of σ-bonded aryl-transition metal compounds to yield biaryls in which some of the aryl groups stem from triarylphosphine ligands [5,6]. Biaryls were also formed from dichlorobis(triphenylphosphine)nickel in the presence of CH_3MgBr [7]. The transfer of a phenyl group from triphenylphosphine to ethyl acrylate to yield ethyl cinnamate has been studied in a detailed report which described the formation of biphenyl from $Ni(PPh_3)(PEt_3)_3$ [8]. Several other reports have described the cleavage of phenyl—phosphorus bonds in triphenylphosphine complexes [9], and some have also established the consequent attachment of the phenyl group to the metal center [10—12]. Hence, given the proper circumstances, the generally inert triarylphosphines may become significantly involved in the reactions of the compound of which they are a part. We describe below one such case.

Results

Methyltris(triarylphosphine)cobalt(I) (Ia, aryl = C_6H_5 [13]; Ib, aryl = 4-CH_3-C_6H_4; Ic, aryl = 3-$CH_3C_6H_4$) decomposes in solutions of THF, benzene, or chlorobenzene to yield biaryls at −20 to 25°C. About 0.8 mole biaryl and one mole of the corresponding triarylphosphine are obtained for each mole of cobalt compound after 24 h, and 0.07 moles of biphenyl per mole of Ia formed after 30 min. No biaryls are found in freshly prepared, solid Ia—c. Reaction mixtures were hydrolysed to facilitate product separation, but identical yields of biaryls were obtained without hydrolysis. Ib yielded 4,4′-dimethylbiphenyl and Ic yielded 3,3′-dimethylbiphenyl and no other isomers were observed.

$$\underset{\text{(I)}}{[(XC_6H_4)_3P]_3CoCH_3} \xrightarrow[\text{(ii) } H_2O,\ HCl]{\text{(i) Decomposition}} XC_6H_4C_6H_4X + (XC_6H_4)_3P + CoCl_2$$

Ia, X = H; Ib, X = 4-CH_3; Ic, X = 3-CH_3;

The reaction is characteristic of the methyl cobalt complexes I. The structurally similar chlorotris(triphenylphosphine)cobalt (II) yields on hydrolysis three equivalents of triphenylphosphine. No biphenyl is formed from reactions of triphenylphosphine with $CoCl_2$ or $Co(acac)_3$ (acac = acetylacetonate) from which I is prepared. Hence, there is no evidence of any general occurrence of cobalt catalyzed decomposition of triphenylphosphine to biphenyl.

Complexing agents interfere with the reaction. No biaryls form in the presence of nitrogen, oxygen or diphenylacetylene, all of which are known to interact with I [14,15,13b]. Although excess triphenylphosphine seems neither to suppress nor to increase the yield of biphenyl, free phosphine is involved in the reaction, since addition of tri-4-tolylphosphine to Ia resulted in formation of mixtures of biphenyl, 4-methylbiphenyl, 4,4′-dimethylbiphenyl and diphenylmethane in the ratios of 16 : 10 : 2 : 1. Crossover experiments of Ia with Ib in about equivalent amounts yielded biphenyl, 4,4′-dimethylbiphenyl and 4-methylbiphenyl in the ratio of 1 : 9 : 4; there was no diarylmethane formed in this case. The biaryls obtained were not accompanied by their isomers. The reactions of Ia with tri-4-tolylphosphine and of Ia with Ib yielded only the para-substituted biaryls. Ic yielded 3 and 3′-substituted biaryls. It follows that the coupling reaction occurred at the site of the carbon—phosphorus bond.

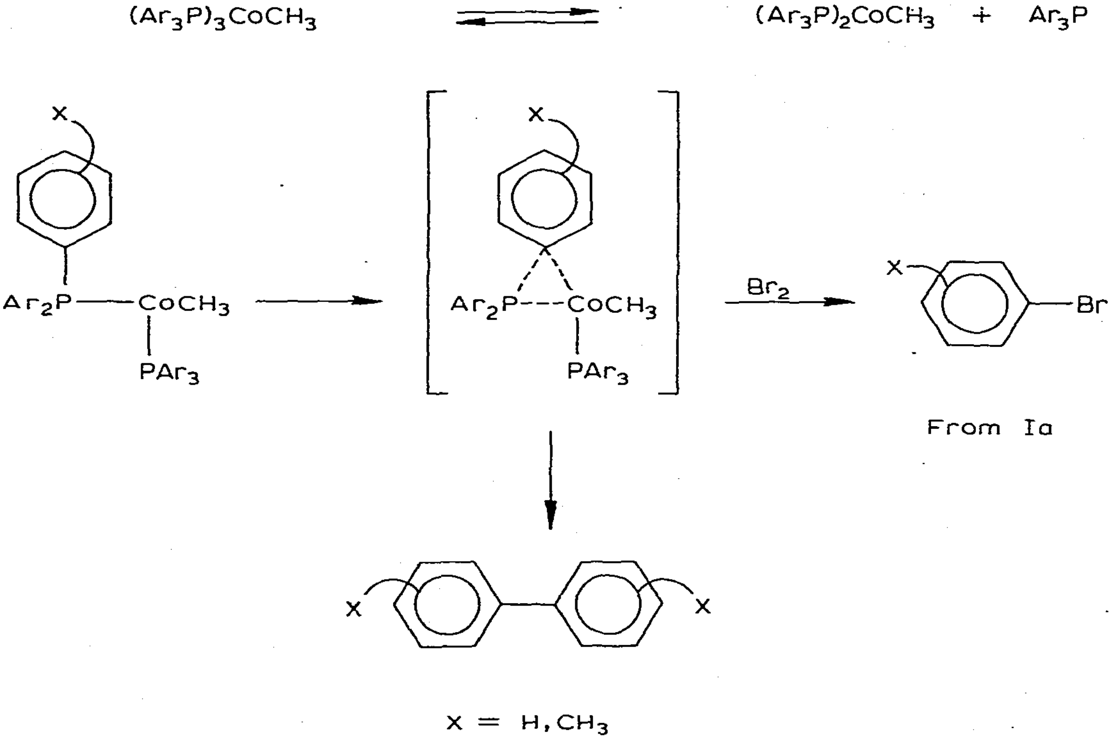
Discussion

Few studies report the direct formation of biaryls from triarylphosphine. Most of these deal with arylmetal σ compounds containing arylphosphine [5,6] or additional reactions with aryl halides [16]. High temperature pyrolysis of triarylphosphine complexes yields biaryls [6,17]. The formation of biphenyl from $Ni[P(C_2H_5)_3]_3[P(C_6H_5)_3]$ and a similar Pd compound in hydrocarbon solutions at 70—125°C [8] was rationalized as an oxidative addition of triphenylphosphine to nickel with intermediate σ-bonded aryl—metal groups. It was not shown that metallation to σ-bonded aryls and the eventual coupling to biaryls actually occurred at the original C—P bond site. By pyrolyzing Pt complexes at high temperature it was demonstrated that formation of arylmetal species from arylphosphine ligands and subsequent formation of biaryls are two distinctively different processes [6]. The low temperature at which I reacts indicates an exceptionally easy and controlled rearrangement of the phosphine group in this compound.

Formation of three biaryls from the reaction of Ia with tritolylphosphine and from the crossover experiments of Ia and Ib indicates the existence of a reversible exchange of phosphine with phosphine ligands of Ia or its partially dissociated product, and between Ia and Ib. ^{31}P NMR measurements on Ia clearly show bands at +26 and —6.3 ppm/H_3PO_4 even at —10°C for bonded and dissociated triphenylphosphine and the presence in the ^1H NMR of two separate absorptions for the methyl-cobalt group indicate at least two forms of I in solution. Hence the phosphine ligand dissociates while the methyl group is still attached to cobalt. II does not release triphenylphosphine in solutions.

Since C—C bond formation occurs exclusively at the site of C—P bond cleavage, the preferred explanation for a rearrangement of I suggests insertion of cobalt into the C—P bond (Scheme 1), i.e., a three-centered oxidative addition [6,8]. Other mechanisms, such as *ortho*-metallation [12,5b] or β-elimination via

SCHEME I



Ia : Ar = C_6H_5 , X = H

Ib : Ar = 4-$CH_3C_6H_4$, X = 4-CH_3

Ic : Ar = 3-$CH_3C_6H_4$, X = 3-CH_3

aryne intermediates [18] can be excluded. *ortho*-Metallation has been shown to occur with cobalt compounds similar to I [4], and has been suggested to occur with I under the present conditions [19], and it is quite likely that I is simultaneously involved in these two independent types of oxidative addition, only the three-centered process leading to biaryls. As Ia partially dissociates a vacant coordination site on the cobalt atom becomes available, and this must be considered a requirement for such an oxidative addition [8]. This also offers a route for interference by foreign complexing agents such as oxygen, nitrogen, and diphenylacetylene. Their attachment to the dissociated cobalt complex seems to block the rearrangement leading to biaryl formation. The quantitative oxidation of the phosphine ligand under oxygen is probably the result of a facile oxidative addition of the latter to I. The negative results with II fit well with this.

It is apparent from the results that the two aromatic rings of each biaryl molecule originate from different phosphine units. This is evident from the high proportions of 4-methylbiphenyl obtained from the reaction of Ia with tritolylphosphine and with Ib. It is also consistent with the observation that I yields nearly 1 mole of biaryl and no more than 1 mole of phosphine while unreacted I, like II, yields 3 moles of phosphine after hydrolysis. The fate of the phosphine residue will be discussed separately [20].

All cases of aryl coupling reactions reported above either started with, or demonstrated an intermediate function of, aryl-metal species. We have as yet been unable to detect or isolate arylcobalt compounds from the reaction mixture, but quenching with bromine of a reaction of Ia in THF solution yielded small amounts of bromobenzene. We propose that an oxidative addition of the carbon phosphorus unit to cobalt is followed by reductive elimination of phenyl cobalt intermediates to form biphenyls. The marked tendency of compound I to undergo oxidative additions is shown by its reactions with CCl_4, $CHCl_3$, and alkyl and aryl halides, and a more detailed mechanism will be discussed separately [21].

Experimental

Materials

Solvents were dried and distilled under Ar before use. Triarylphosphines were freshly crystallized from ethanol. Trimethylaluminum (Ethyl Corporation) was used in THF solutions. Authentic 3- and 4-methylbiphenyl [22], 4,4'- and 3,3'-dimethylbiphenyl [23] were prepared for comparison. Tri-4-tolylphosphine and tri-3-tolylphosphine were prepared by standard methods [24].

Instrumentation

GLC was carried out at 145°C on 10% Apiezone L and Silicon SE-30 Cu columns for separation of the phosphines (which do not show GC peaks) and the biphenyl homologs, and on 20% PMPE (polymetaphenyl ethers) at 190°C for the separation of isomers of dimethylbiphenyls [25]. NMR spectra were recorded on Varian HA-100 and Bruker 270 MHz and 37.4 MHz (^{31}P) spectrometers. Mass spectra were recorded on Varian MAT 311 and Varian MAT 112 GC-MS instruments, the latter with a 3% SE-30 column.

Reactions of methyltris(triarylphosphine)cobalt(I) (Ia, aryl = C_6H_5; Ib, aryl = 4-$CH_3C_6H_4$; Ic, aryl = 3-$CH_3C_6H_4$;)

Compounds Ia—c were prepared as described for Ia [13]. All were reddish brown solids similar to Ia, but Ib and Ic were more soluble in THF and aromatic solvents. The solid compounds did not contain biaryls. While Ia proved stable enough to be washed and dried repeatedly, Ib and Ic had to be used as crude precipitates, dried after being washed with ether.

Ib, Found: C, 76.8; H, 5.8; P, 6.0. Ic, Found: C, 76.5; H, 6.2; P, 6.5%. $C_{64}H_{66}CoP_3$ calcd.: C, 77.62; H, 6.80; Co, 9.4; P, 5.98%. Like Ia, both react with CCl_4 to give a blue complex [15] and solutions decompose in acids to give free phosphine. Solids Ia—c do not decompose in water, but their solutions in $CHCl_3$ decompose in water instantaneously, yielding phosphine and aq. $CoCl_2$. Ib (0.5 g) yielded tritolylphosphine 0.38 g, Ic (0.69 g) yields trilolylphosphine (0.6 g).

The ^{31}P NMR spectrum of Ia in THF at 263° K shows ^{31}P (ppm, H_3PO_4): —6.28 (Free Ph_3P) and 25.8 (complexed Ph_3P) relative integrals 14 : 10. By warming to 298° K the integral ratio increases to 46 : 10. ^1H NMR of I in THF and in toluene-d_6 shows two broad singlets at δ (ppm, TMS) —0.4 and —1.3 (CH_3—Co, broadening expected by Co quadrupole relaxation, signals disappear upon warm-up and decomposition by air or addition of PhC≡CPh and other reactants [20]) and 7.0 (aromatic), ratio 5.5 : 1 to combined high field signals).

The cobalt compound Ia, Ib or Ic (4.4 mmol), was dissolved under Ar in THF or chlorobenzene (50 cm^3) at —20° C (CCl_4/CO_2 slush) and the solution allowed to warm up to 25° C with stirring. Hydrolysis wih aq. HCl (pH 3—4) for 24 h and extraction with $CHCl_3$ were followed by chromatography on a silica gel column with hexane. The mixture of organic eluants was treated with iodine to oxidize phosphines [26]. Repeated chromatography with hexane yielded the corresponding biaryls. Phosphine oxide was next eluted with $CHCl_3$.

The reactions of 3.8 g (4.4 mmol) of Ia yielded 0.4—0.55 g (2.5—3.5 mmol) biphenyl and 1.2 g (4.3 mmol) triphenylphosphine oxide. 5.4 g (5 mmol) of Ib yielded 0.65 g (3.5 mmol) of 4,4′-dimethylbiphenyl, m.p. 121° C, with 1.4 g (4.3 mmol) tri-4-tolylphosphine oxide, m.p. 142—3° C (lit. 135° C [23]), 5 g (4.6 mmol) Ic yielded 1.4 g tri-3-tolylphosphine oxide, m.p. 110° C (lit. 111° C [23]) and 0.6 g (3.3 mmol) of colourless, liquid 3,3′-dimethylbiphenyl. These products were identical (GLC, NMR, m.p. and mixed m.p.) with authentic compounds.

An identical run with Ia was carried out without hydrolysis. Biphenyl was isolated as above (0.4 g). Another run with Ia, carried out at —20° C and quenched after 30 min, yielded 0.05 g of biphenyl.

Reaction with chlorotris(triphenylphosphine)cobalt (II) [26]

Several runs were carried out between —20 and 25° C and a single run was carried out under reflux (in THF). The green complex II (1 g, 1.2 mmol) was dissolved and kept in THF (20 cm^3) under argon or under oxygen for 6 h. The solution gradually turned blue under argon, but became black immediately under oxygen, or under reflux. After hydrolysis as above, triphenylphosphine (0.9 g, 3.44 mmol) and traces of triphenylphosphine oxide (identified by TLC on silica with chloroform) were the only products. In no case was formation of biphenyl detected. No ^{31}P NMR band could be observed with II. Added Ph_3P shows a broad absorption at —7 ppm.

Reactions of Ia under nitrogen and under oxygen

Reactions of Ia (3.8 g, 4.4 mmol) were carried out as above in THF and in chlorobenzene under an atmosphere of nitrogen or oxygen, and quenched after 24 h. The only products were triphenylphosphine (2.4 g, 9.2 mmol, recrystallized) with nitrogen and triphenylphosphine oxide (2.6 g, 9.4 mmol, recrystallized) with oxygen (no traces of triphenylphosphine).

Reactions of Ia with diphenylacetylene

To a solution of diphenylacetylene (0.7 g, 4.4 mmol) in THF (50 cm^3) under argon, Ia (4.4 mmol) was added at —20°C and allowed to react as above. The products [13b] contained no biphenyl.

Reactions of Ia with triarylphosphines

Ia (4.4 mmol) and triphenylphosphine (5 g, 20 mmol) reacted in THF (50 cm^3) as above. Biphenyl was isolated (0.45 g, 2.9 mmol).

Ia (4.4 mmol) and tri-4-tolylphosphine (0.92 g, 3 mmol) in THF (50 cm^3) yielded (GLC elution order); biphenyl, diphenylmethane, 4-methylbiphenyl and 4,4'-dimethylbiphenyl in the ratio (GLC) of 16 : 1 : 10 : 2, (0.51 g combined yield).

Reaction of Ia with Ib

Equivalent amounts (~4.4 mmol each) of Ia and Ib were mixed in THF (100 cm^3) at —20°C, left up to 24 h and treated as above. Products were biphenyl, 4-methylbiphenyl and 4,4'-dimethylbiphenyl in the ratio (GLC) of 1 : 4 : 9 (1 g combined yield).

Attempted reaction of triphenylphosphine with $CoCl_2$ and with $Co(acac)_3$

Triphenylphosphine (1.0 g, 3.8 mmol) and an equivalent amount of $CoCl_2$ or $Co(acac)_3$ were mixed in THF (20 cm^3) under Ar and treated as in the reactions of I. Only triphenylphosphine (1.0 g) was obtained.

Reaction of Ia with bromine

A solution of Ia (0.2 g, 0.23 mmol) in THF (25 cm^3) was kept at —20° for 2 h. Bromine (0.04 g, 0.5 mmol) in THF (10 cm^3) was added dropwise and the mixture (colour change from pink to green) allowed to reach room temperature (1 h) and hydrolyzed. Organic products were extracted with 10 cm^3 diethylether. Analysis by GC-MS showed the presence of bromobenzene (less than 0.01 mmol).

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