Journal of Organometallic Chemistry, 182 (1979) 555—559

REACTIONS OF METHYLTRIS(TRIARYLPHOSPHINE)COBALT

II *. REARRANGEMENT OF TRIARYLPHOSPHINE AND OXIDATIVE ADDITIONS OF ARYL HALIDES

SOPHIA NUSSBAUM and MICHAEL MICHMAN *

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

(Received June 8th, 1979)

Summary

Solutions of $[(C_6H_5)_3P]_3CoCH_3$ (I) in C_6H_5Cl yield biphenyl, triphenylphosphine, methyldiphenylphosphine and diphenylphosphine. In $4\text{-}ClC_6H_4CH_3$, 4-methylbiphenyl and 4,4'-bitolyl form as well. Solutions of I in C_6H_6, C_6D_6, $C_6H_5CH_3$, C_6H_5Br yield only triphenylphosphine and biphenyl, while in $4\text{-}FC_6H_4I$ 4,4'-difluorobiphenyl is formed but no biphenyl. The cobalt compound is recovered as $(Ph_3P)_nCoX$ or as CoX_2 (X = Cl, Br, I, n = 3 or 2) from reactions with arylhalides. The results are rationalized in terms of the very strong tendency for I to undergo oxidative addition reactions.

We recently described the decomposition of $(Ar_3P)_3CoCH_3$ (I) ($Ar = C_6H_5$; $4\text{-}CH_3C_6H_4$; $3\text{-}CH_3C_6H_4$) in THF and C_6H_5Cl solutions at low temperatures to yield the corresponding biaryls ArAr [1]. It was suggested that triarylphosphine in I rearranged by a three-centered oxidative addition with consequent coupling to biaryl by reductive elimination from a proposed σ-arylcobalt intermediate. Evidence was based on the conditions for biaryl formation, distribution of isomers, interference by complexing agents and crossover experiments. Reactions of I with arylhalides and analysis of phosphines recovered from this reaction now provide further support for this rationalization, and point to an unusual rearrangement of the phosphine group.

Results and discussion

I was brought into reaction in a number of aromatic solvents and the results as analyzed by GC-MS are listed in Table 1. C_6D_6 did not give any deuterated

---

* For part I see ref. 1.

TABLE 1

ORGANIC PRODUCTS FROM REACTION OF I WITH AROMATIC SOLVENTS

Solvent	Products			
C_6H_6; C_6D_6	biphenyl	—	—	triphenylphosphine
$C_6H_5CH_3$	biphenyl	—	—	triphenylphosphine
C_6H_5Cl	biphenyl, diphenylphosphine, methyldiphenylphosphine,			triphenylphosphine
C_6H_5Br	biphenyl	—	—	triphenylphosphine
FC_6H_4I	—	4,4'-difluorobiphenyl	—	triphenylphosphine
$CH_3C_6H_4Cl$ [a]	biphenyl, diphenylmethane, 4-methylbiphenyl, 4,4'-bitolyl, diphenylphosphine, methyldiphenylphosphine			triphenylphosphine

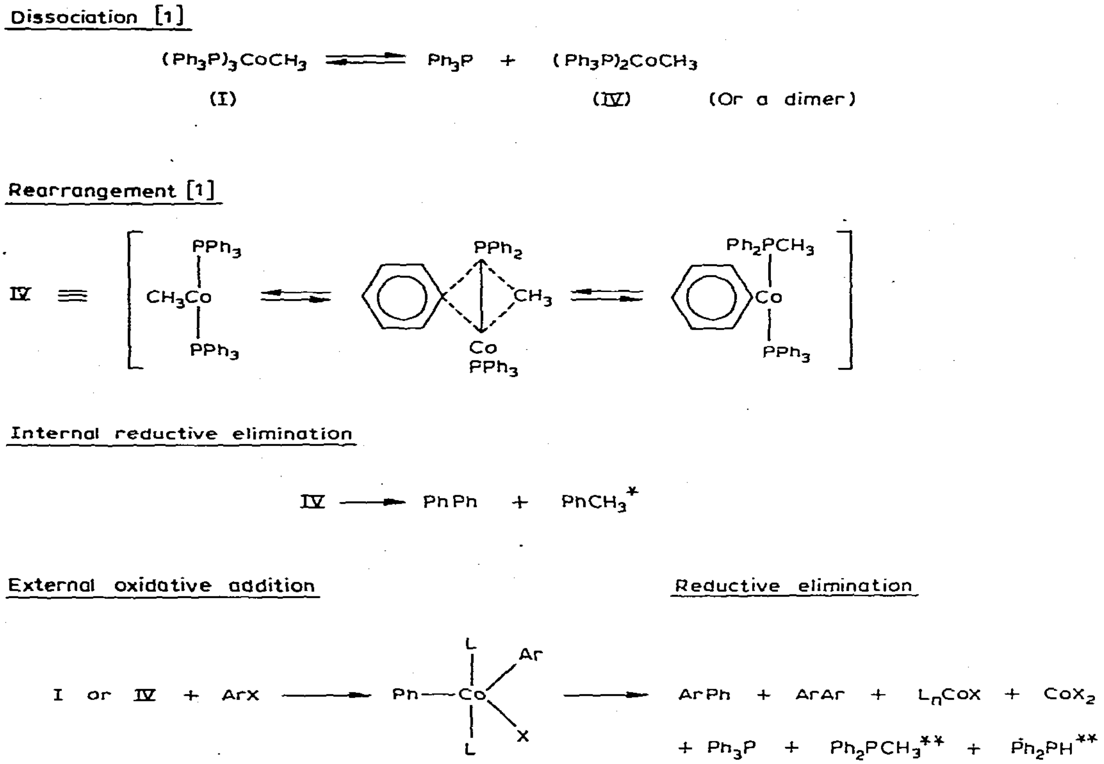
[a] Traces of *m/e* 182 and 196 detected by mass spectroscopy only.

biphenyl, 4-FC_6H_4I yielded difluorobiphenyl but no biphenyl. The reaction of I with C_6H_5Cl, $CH_3C_6H_4Cl$, C_6H_5Br, FC_6H_4I and other haloaromatic compounds also yielded $(Ph_3P)_3CoX$ (II) (X = Cl, Br, I), $(Ph_3P)_2CoX$ (III) and CoX_2. With C_6H_5Cl, more than 24 h at room temperature, were needed to give detectable amounts of II. In $CH_3C_6H_4Cl$, II and III formed within 3—4 h, while in C_6H_5Br and FC_6H_4I reaction was immediate showing an instantaneous colour change from red to green. In these two cases the reactions went as far as $CoBr_2$ or CoI_2 and free phosphine.

The results with 4-$CH_3C_6H_4Cl$ are the most revealing. Both II, III and 4,4'-bitolyl are apparently the products of an oxidative addition of the solvent to I or to dissociated I (IV) (Scheme 1) in a manner often observed for such cases [2], and which fits the order of reactivity I >> Br > Cl, followed by reductive elimination. Methylbiphenyl results from an effective combination of two processes: addition of $CH_3C_6H_4Cl$ to I and the above mentioned rearrangement of triphenylphosphine in I. This observation further reinforces earlier indications [1] that the latter rearrangement involves σ-bonded phenylcobalt intermediates. (It should be noted that this implies that biphenyl from the reactions in C_6H_5Cl is also a "crossed" product.) Formation of diphenylmethane and the products of *m/e* 182 and 196 which may be benzyltoluene and bitolylmethane could imply insertion into methyl C—H bonds of chlorotoluene. However, as shown previously, diphenylmethane is also formed in reactions carried out in THF [1], and the present results show that, at least with $C_6H_5CH_3$ and C_6D_6, C—H bond cleavage in the solvent does not occur. The probable source of methylene is the methyl group bonded to cobalt.

Most surprising is the formation of Ph_2PCH_3 and Ph_2PH in C_6H_5Cl and $CH_3C_6H_4Cl$. This suggested that the proposed 1,2 shift of a phenyl group from phosphorus to cobalt is accompanied by a similar 1,2 shift of the methyl group from cobalt to phosphorus. Precedents for such a process are not available to the best of our knowledge, but a cobalt trimethylphosphine complex with a fluxtional three centered-cobalt, phosphorus, carbon-structures has been described [3], and may be analogous to the present case. Our reaction may be related to the concerted double 1,2 shifts recently reviewed and categorized as "dyotropic shifts" [4] although there is no evidence for this. The "dyotropic

SCHEME 1. SEVERAL POSSIBILITIES OF OXIDATIVE ADDITIONS WITH I



L = Phosphine ligand ; Ar = aryl group.

* The formation of toluene has been claimed [7]

** In C_6H_5Cl and $CH_3C_6H_5Cl$

shifts" include examples of shifts in organometallic complexes of iron and cobalt.

Diphenylphosphine could form from similar hydride shifts. Hydridocobalt species are likely to be present as a result of α elimination from the cobalt bonded methyl [5], (e.g., formation of diphenylmethane), or possibly from β metallation of the phosphines [6].

It seems that in C_6H_5Cl and $CH_3C_6H_4Cl$ the various competitive processes are balanced in such a way as to yield all the possible products. In C_6H_5Br and FC_6H_4I the oxidative addition by solvent to I is extensive enough to yield II, III, CoX_2 along with triphenylphosphine and either biphenyl or difluorobiphenyl as the exclusive organic products. Since with II, rearrangement of the phosphine ligand does not occur [1], formation of biphenyl or fluorobiphenyl in FC_6H_4I or of rearranged phosphines in FC_6H_4I and C_6H_5Br cannot be expected. The absence of rearranged phosphines in C_6H_6 and $CH_3C_6H_5$ is not yet understood.

In Scheme I the results are rationalized in terms of a series of the various oxidative additions which we believe represent the dominant feature in the chemistry of I. Dissociation of I, which was demonstrated by ^{31}P and ^{1}H NMR studies [1], yields a coordinatively unsaturated species (IV) (perhaps as a dimer), which should be highly prone to oxidative addition either internally by the shift of phosphine ligands and methyl groups or externally by reaction with solvents.

Several aspects of the chemistry of I have been described elsewhere [7,8], but were left partially unexplained; for example, the formation of toluene and benzene in appreciable yields. The course of reactions proposed in Scheme I suggests that their formation is similar to that of biphenyl. The observation that toluene is formed in preference to benzene is also in agreement with our observations that hydrogen transfer takes place to a smaller extent, as concluded from the ratios Ph_2PCH_3/Ph_2PH. The account presented here outlines the main features in the chemistry of I, but obviously individual cases must be further studied. Variations in experimental conditions may also strongly influence the nature of the cobalt-containing residues which are eventually isolated.

Experimental

General

All reactions were run under argon with dry solvents and equipment. GC tests were carried out on a Baker 720 chromatograph, GC-MS on a Varian MAT 12 spectrometer with electron ionization at 70 eV. Copper tube columns on which phosphines were eluted in very broad undetectable peaks [1] were replaced by glass and teflon columns, charged with 10% SE-30 at 160°C.

Reaction of I with aromatic and haloaromatic solvents

A sample of dry I [1] (~3—5 g) was dissolved in the corresponding solvent (3 fold molar excess) at —20°C and kept under stirring at room temperature for 24 h. The mixture was hydrolysed with 2.2 N HCl and the organic products extracted with hexane and dried. The extract was chromatographed on a silica column, 2.5 × 10 cm, to separate cobalt salt residues and three fractions of hexane eluant, 300 cm^3 ea., collected. The products were mostly concentrated in the first one together with unreacted aromatic solvent.

a. C_6H_5Cl: Analysis by GC and GC-MS (as below) showed the formation of biphenyl, triphenylphosphine, diphenylphosphine and methyldiphenylphosphine in molar ratios of ~1 : 1 : 0.2 : 0.1. In several runs the formation of small quantities of the green compound $(Ph_3P)_3CoCl$ was observed after 24 h.

b. $4\text{-}CH_3C_6H_4Cl$: The product mixture separated on 10% SE-30 at 160°C, 35 cm^3 min^{-1} showing relative retention volumes: biphenyl (370), diphenylmethane (455), 4-methylbiphenyl (585), traces of *m/e* 182 (595), diphenylphosphine (760), 4,4′-bitolyl (890), traces of *m/e* 196 (900), methyldiphenylphosphine (1000). [The normalized value of 1000 equals 35 min at the mentioned conditions.] Molar ratios in that order were 3 : 0.5 : 1 : trace : 0.4 : 1 : trace : 1.5. Triphenylphosphine was eluted last after elevating column temp. to 185°C. Peak intensities were corrected by calibration curves to obtain molar ratios. All compounds were compared (retention time and mass spectrum) with authentic materials. The phosphines were further identified by TLC on silica plates with $CHCl_3$ and $CHCl_3/C_2H_5OH$ as solvents.

The mass spectral data of the products are as follows (*m/e* (rel. int.)): Biphenyl: 155 (12); 154* (100); 153 (42); 152 (28); 76 (15); Diphenylmethane: 169 (10); 168* (100); 166 (20); 165 (50); 164 (10); 155 (5); 154 (30); 153 (54); 152 (50); 151 (5); 138 (5); 128 (5); 115 (10); 91 (25); 76 (10). Methylbiphenyl: 169 (15); 168* (100); 167 (85); 166 (10); 165 (31); 154 (5); 153 (25); 152 (28); 151 (6); 141 (4); 139 (5); 105 (11); 91 (7); 77 (3); 76 (45). Diphenylphosphine: 188 (1.7); 187 (4.4); 186* (32); 183 (7); 152 (6); 109 (9); 108 (100); 107 (43); Bitolyl: 183 (19); 182* (100); 181 (44); 168 (12); 167 (94); 166 (44); 165 (63); 153 (12); 152 (31); 151 (6). Methyldiphenylphosphine: 201 (60); 200* (75); 199 (38); 185 (50); 184 (15); 183 (100); 152 (48); 121 (23); 115 (17); 107 (17); 92 (21); 91 (22); 77 (20); 76 (50).

c. C_6H_6, $C_6H_5CH_3$, C_6D_6: The only products recovered were biphenyl and triphenylphosphine. No deuterium containing products were detected from C_6D_6.

d. C_6H_5Br: Only biphenyl and triphenylphosphine were observed.

e. FC_6H_4I: The only product detected in GC and GC-MS was 4,4′-$FC_6H_4C_6H_4F$. *m/e* (rel. int.): 191 (20); 190* (100); 189 (40); 188 (33); 95 (20); 94 (28); ^{1}H NMR δ (ppm): 6.92 (triplet, J 9 Hz), 7.3 (quartet, J 7 Hz and 2 Hz, aromatic AB further split by ^{19}F).

Cobalt containing products

Small amounts of a green precipitate formed from reactions in C_6H_5Cl after 24 h or more. Larger amounts formed in $CH_3C_6H_4Cl$ after 3—4 h. and immediate quantitative transformation of I to a green precipitate took place in C_6H_5Br and FC_6H_4I. To isolate the products, the reaction mixtures were filtered under Ar without hydrolysis and the solids washed with ether. Extractions with cold ethanol separated a green residue of $(Ph_3P)_3CoX$ (II) [9] or $[(Ph_3P)_2CoX]_n$ (III) X = Cl, Br, $n \geqslant 2$, and a blue solution which on evaporation yielded large crystals of triphenylphosphine and CoX_2 (X = Br, I) in the blue ethanol saturated form, which in water dissolved to yield the pink CoX_2 form. The yields and relative quantities of II, III and the cobalt salt varied in different runs.

From C_6H_5Cl and $CH_3C_6H_4Cl$, mostly II was detected, but the green cobalt complex from C_6H_5Br was mainly III. Found: C, 64.7; H, 4.85; Br, 11.8; P, 10.2; $C_{36}H_{30}P_2CoBr$ calcd.: C, 65.0; H, 4.5; Br, 12.0; P, 9.5%. From FC_6H_4I mostly cobalt iodide and phosphine were collected after ethanol washing.

Acknowledgement

The authors thank Mrs. P. Ovadia of The Ben Gurion University of the Negev for GC-MS analyses.

References

1 M. Michman, V.R. Kaufman and S. Nussbaum, J. Organometal. Chem. 182 (1979) 547.
2 P. Fitton and E.A. Rick, J. Organometal. Chem., 28 (1971) 287.
3 H.H. Karsch, H.-F. Klein and H. Schmidbaur, Angew. Chem., 87 (1975) 630.
4 M.T. Reetz in R. West and F.G.A. Stone (Eds.), Adv. Organometal. Chem., Vol. 16, Academic Press, New York, 1977, 33.
5 L.S. Pu and A. Yamamoto, J. Chem. Soc. Chem. Commun., (1974) 9.
6 G.W. Parshall, Acc. Chem. Res., 6 (1975) 113.
7 F.S. Dyachkovskii, N.E. Krusch and A.E. Shilov, Zhur. Obschei. Khim., 40 (1979), 1926 (J. Gen. Chem., 40 (1970) 1712).
8 M. Michman and L. Marcus, J. Organometal. Chem., 122 (1976) 77.
9 M. Aresta, N. Rossi and A. Sacco, Inorg. Chim. Acta, 3 (1969) 227.