INTERFERENCE BY PHOSPHINE DECOMPOSITION IN OXIDATIVE ADDITIONS OF ARYL HALIDES TO METHYL- , AND TRIMETHYLSILYL-TRIS(TRIPHENYLPHOSPHINE)COBALT

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Summary

The oxidative addition of aryl halides, ArX, to $[Ph_3P]_3CoCH_3$ yield ArAr and $ArCH_3$ when $Ar = 4\text{-}CH_3C_6H_4$, but exclusively $ArCH_3$ for 1- and 2-bromonaphthalene and 4-bromobiphenyl. Decomposition of the phosphine ligand in $[Ph_3P]_3CoCH_3$ interfers with these reactions to varying extents depending on the relative rates of the reactions; ArCl mostly gives PhPh with some ArPh and ArAr; ArI gives mostly ArAr; ArBr shows intermediate behaviour. Other cobalt compounds such as $[Ph_3P]_3CoSi[CH_3]_3$, $[Ph_2PCH_3]_3CoCH_3$, $[Ph_2PCH_3]_3CoPh$ and $[Ph_2PGe(CH_3)_3]_3CoCH_3$ and several other organic halides examined show a low activity in the oxidative addition.

Increasing attention has recently been given to cases of carbon–phosphorus bond cleavage in triaryl phosphine ligands attached to transition metals. As a result of such cleavage, arylated side products were noted on several occasions in which phosphine-bearing homogeneous catalysts were employed [1]. The extent to which such reactions interfere with the expected activity of a catalyst under a given set of conditions is an interesting question [2].

A facile cleavage of carbon–phosphorus bonds has been observed with $[Ph_3P]_3CoCH_3$ and several of its analogues are discussed in detail [3,4]. The tendency of $[Ph_3P]_3CoCH_3$ to react with aryl halides by oxidative addition, provides an opportunity of studying the competition between this reaction and phosphine decomposition. Some observations on the relative reactivities of the cobalt-bonded methyl group in $[Ph_3P]_3CoCH_3$ and the trimethylsilyl group in $[Ph_3P]_3CoSi(CH_3)_3$ are also considered, and a comparison with several other cobalt compounds and other organic halides is made.

Results and discussion

The reactions of $[Ph_3P]_3CoCH_3$ with 4-halotoluenes give a range of products as follows:

$$ArX + [Ph_3P]_3CoCH_3 \rightarrow PhH + PhPh + PhAr + ArAr + PhCH_3 + ArCH_3$$

$$(Ar = 4\text{-}CH_3C_6H_4\text{-}; \; X = Cl, \; Br \; or \; I)$$

Aryl fluorides are unreactive [3b].

Runs were carried out in toluene solutions with 2-methylnaphthalene as internal standard. The results are shown in Table 1; amounts of products are given in mmoles, so that yield based on cobalt compound can be seen. There are considerable differences in rates and product ratios, that are apparently related to the relative reactivity of aryl halides. The iodide reacts so rapidly as to leave little opportunity for any phosphine cleavage, whereas biphenyl is the main product with the slow reacting chloride. The differences are also evident from the colour change. A change from pink for a phosphine methylcobalt compound to green for a cobalt phosphine halide is immediate with 4-iodotoluene, but takes ~ 4 h with 4-bromotoluene and is incomplete after 24 h with 4-chlorotoluene. A rough estimate of relative rates for the two types of the overall reactions can be made: for X in aryl $= Cl, Br, I, V(PhPh)/V(ArAr) = \sim 50, \sim 0.25, \ll 10^{-2}$, respectively.

Yields of the cross-products in each of these cases reflect the same order. Subsidence of the reactions, as indicated by the leveling-off of the yield gradient

TABLE 1

REACTION PRODUCTS OF $[Ph_3P]_3CoCH_3$ WITH 4-HALOGENOTOLUENE

$[Ph_3P]_3CoCH_3$ (mmol)	4-Halogeno-toluene (X/mmol)	Time (h)	PhPh (mmol)	ArPh[a] (mmol)	ArAr (mmol)
1.5	Cl	0.5	0.015	0	0
		3	0.28	0.004	0
		5.3	0.45	0.005	trace
		9	0.64	0.03	0.002
		12	0.65	0.06	0.013
		24	0.67	0.06	0.013
2.0	Br	0.5	0	0	0
		1	0	0.015	0.007
		2	0.007	0.08	0.019
		3	0.015	0.16	0.075
		4	0.013	0.16	0.06
		10.5	0.012	0.14	0.04
		24	–	0.2	0.05
2.0	I	0.1	0	0.07	0.05
		0.25	0	0.09	0.21
		0.5	0	0.07	0.25
		1	0	0.06	0.5
		4	0	0.07	0.9
		8.5	0	0.06	1.04
		24	0	0	0.98

[a] $Ar = 4\text{-}CH_3C_6H_4$.

may also serve as an indicator. With 4-chlorotoluene, maximum yields are reached at the end of ~ 12 h for all three products. With 4-iodotoluene, phosphine decomposition subsides within 10 min, while the coupling of 4-iodotoluene continues for ca. 4 h.

Apparently oxidative addition of aryl halides is followed by reductive dimerization of the aryl residues, and the interception by the phenyl residue from triphenylphosphine occurs between those stages.

C–P bond cleavage may also involve oxidative addition as suggested earlier [3]. Addition and coupling of aryl halides may consist of two discrete steps, a point which is not easy to verify. Dimerization may be regarded as irreversible, and seems to be faster than the addition of aryl halides. This fits with the very pronounced reactivity differences between the aryl halides and the fact that the reactivities fall in the expected order ArI > ArBr > ArCl $\gg$ ArF [5]. Hence, relative yields of PhPh and ArAr reflect the competition between the addition of an aryl halide and that involving phosphine cleavage. The presence of substantial amounts of the cross-product ArPh further corroborates the implication [3] that some intermediate is common for the two reaction pathways.

Aryl-methyl coupling also occurs. In the reactions of halogenotoluenes yields of p-xylene do not exceed 10% of the combined yield of biaryls. This pattern is completely reversed when 1-bromobiphenyl or 1- and 2-bromonaphthalene are used: with these coupling with the cobalt bonded methyl group is almost exclusive (Table 2). No phenylation of the aryl groups or biphenyl or biaryl formation are detected in these cases.

The selectivity of the coupling of aryl halides with metal-bonded methyl and phenyl groups has been considered before, e.g. in connection with Ni compounds in which coupling by direct thermolysis was distinguished from a radical chain reaction induced by oxidative additions of aryl halides [6]. We believe that the present results reflect a different influence, that of steric constraints, which possibly differ for intra- and inter-molecular reactions.

Many metal complexes formed as a result of phosphine decomposition, have been identified as dimers with μ-PPh$_2$ bridges [7–10]. Dissociation of Ph$_3$P from the 16 electron [Ph$_3$P]$_3$CoCH$_3$ [3] necessarily yields a highly unsaturated complex which could be expected to dimerise. In our work, for the reactions involving bromobenzene and bromotoluene only, we isolated substance showing the composition ([Ph$_3$P]$_2$CoBr)$_n$ with $n \geqslant 2$. Biaryls from [Ar$_3$P]$_3$CoCH$_3$ have been previously shown

TABLE 2

METHYLATION PRODUCTS FROM REACTIONS OF [Ph$_3$P]$_3$CoCH$_3$ WITH ARYL HALIDES

Reactant	Product	Yield (% based on Co)
Chlorobenzene	Toluene	5–10
Bromobenzene	Toluene	5
4-Chlorotoluene	p-Xylene	5–10
4-Bromotoluene	p-Xylene	5–10
4-Bromobiphenyl	4-Methylbiphenyl	70 [a]
1-Bromonaphthalene	1-Methylnaphthalene	100 [a]
2-Bromonaphthalene	2-Methylnaphthalene	72 [a]

[a] Only product.

TABLE 3

REACTIONS OF [Ph$_3$P]$_3$CoCH$_3$ WITH ALKYL HALIDES OR BROMOPYRIDINES

[Ph$_3$P]$_3$CoCH$_3$ + 2-bromopyridine → biphenyl + 2,2'-bipyridyl ~ 1/1	> 1%
[Ph$_3$P]$_3$CoCH$_3$ + 3-bromopyridine → biphenyl + 3,3'-bipyridyl ~ 1/2	> 1%
[Ph$_3$P]$_3$CoCH$_3$ + 1-chlorooctane → − + N-nonane	~ 5% [a]
[Ph$_3$P]$_3$CoCH$_3$ + 2-bromooctane → − + 2-methyloctane	~ 8% [a]

[a] GC signal area relative to that of original alkyl halide. Yield based on aryl (alkyl) halide, which is in three-fold excess over the cobalt compound.

to contain aryl groups originating from different Ar$_3$P units [3]. All this can be rationalised by assuming an intermolecular reaction through a binuclear intermediate. However, no such aggregation is required if the oxidative addition is followed by coupling with the CoCH$_3$ group; in the absence of mechanistic detail we assume that the propensity of bulky aryl halides to take part in such a process is due to hindered aggregation and a preference for an intramolecular pathway. (The reason why 4-bromobiphenyl reacts in this way is less clear, as it should not be more bulky than halogenotoluenes.) Absence of phenylation in these cases is also in accord with this view.

Several other halides gave coupling in low yields in reactions with [Ph$_3$P]$_3$CoCH$_3$. Bromopyridines gave some coupling, and 1-chlorooctane and 2-bromooctane coupled with the cobalt-bonded methyl group in low yield (Table 3). No biphenyl or phenylation were detected in the last two cases.

Experiments with [Ph$_3$P]$_3$CoSi[CH$_3$]$_3$ show this compound is much less reactive than the methylcobalt compound under comparable conditions, as in keeping with general observations on silyl-transition metal derivatives [11]. Autodecomposition is negligible at 20°C, and comparable to that of [Ph$_3$P]$_3$CoCH$_3$ only at 80°C. Oxidative additions are observed with 2-bromonaphthalene at 80°C but not with 4-chlorotoluene or 4-bromotoluene. The reaction with 2-bromonaphthalene yields 2-trimethylsilylnaphthalene and no coupling of the naphthyl residue is detected. However, formation of low yields of PhSi(CH$_3$)$_3$ may be taken as evidence for a little phosphine cleavage (Table 4).

Other compounds such as [Ph$_2$PCH$_3$]$_3$CoCH$_3$, [Ph$_2$PCH$_3$]$_3$CoPh or [Ph$_2$PGe-(CH$_3$)$_3$]$_3$CoCH$_3$ gave no products of oxidative addition when treated with 4-chloro- and 4-bromo-toluene or 2-bromonaphthalene although they did yield products of decomposition of the phosphine ligand [4].

TABLE 4

REACTIONS OF [Ph$_3$P]$_3$CoSi[CH$_3$]$_3$ IN VARIOUS SOLVENTS OR WITH ARYL HALIDES

Solvent	Temperature (°C)	Time (h)	Products identified			Ratio
THF	20	48	PhH	PhPh	PhSi(CH$_3$)$_3$	trace: 1/1
THF	50	0.75	−	PhPh	PhSi(CH$_3$)$_3$	−: 3/1
4-Chlorotoluene	20	48	−	PhPh	−	
2-Bromonaphthalene	20	48	−	−	−	− −
2-Bromonaphthalene	80	0.5	−	−	C$_{10}$H$_7$Si(CH$_3$)$_3$	25 [a]/1
2-Methylnaphthalene	80	0.5	−	PhPh	PhSi(CH$_3$)$_3$	30 [a]/2/1

[a] Ratio of solvent to products from GC peak area.

Experimental

General

Reactions with cobalt compounds were carried out under argon. The preparations of the compounds used were described recently [4].

In a typical experiment a sample of $[Ph_3P]_3CoCH_3$ (3–5 g, 3.5–5.8 × 10^{-3} mol) in the form of dry, pink powder was dissolved in an excess of the corresponding aryl halide at 20°C or as specified in the tables. For rate measurements the $[Ph_3P]_3CoCH_3$ and halogenotoluene were added to 20 ml toluene at 25°C containing 2-methylnapthalene (0.071 g, 0.5 mmol) as internal standard. Hydrolysis with 8% aqueous HCl, was followed by extraction with hexane and drying over anhydrous $MgSO_4$. The organic phase was washed 4–5 times with 0.1 N aqueous KI/I_2 and eluted from a silica column 2.5 × 10 cm with hexane to remove the phosphine quantitatively as phosphine oxide as well as residues of cobalt compounds. The products were analysed by GC and GC/MS on 10% SE30.

Reaction with 4-chlorotoluene. $[Ph_3P]_3CoCH_3$ (1.29 g, 1.5 mmol) and 4-chlorotoluene were treated as above. During 24 h there was a colour change from pink to brown.

Reaction with 4-bromotoluene. $[Ph_3P]_3CoCH_3$ (1.72 g, 2 mmol) and 4-bromotoluene (11.3 mmol) were treated as above. A green precipitate appeared after 1 h, and after 10 h the mixture was bright green.

Reaction with 4-iodotoluene. $[Ph_3P]_3CoCH_3$ (1.72 g, 2 mmol) and 4-iodotoluene (11.3 mmol) were treated as above. A green precipitate formed immediately. No satisfactory analysis was obtained because the sample contained triphenylphosphine and CoI_2.

Reaction with 1-bromonaphthalene. $[Ph_3P]_3CoCH_3$ (2 mmol) was mixed with 1-bromonaphthalene (8 ml, 60 mmol) at 10°C for 24 h. The colour changed to green within minutes. Work-up as above, gave 1-methylnaphthalene (100% based on cobalt), and naphthalene, but no biphenyl. GC/MS: m/e 142(2413); 141(4600); 128(2641); 127(4098).

Reaction with 2-bromonaphthalene. A mixture of $[Ph_3P]_3CoCH_3$ (1 mmol), 1-bromonaphthalene (2 mmol, 0.41 g) and 10 ml benzene was kept at 10°C for 24 h. The colour changed to dark yellow and after 24 h 2-methylnaphthalene was the sole product (72% based on cobalt). No biphenyl was detected.

Reaction with 4-bromobiphenyl. $[Ph_3P]_3CoCH_3$ (1 mmol) was mixed with 4-bromobiphenyl (2 mmol, 0.45 g) in 20 ml benzene at 10°C. The mixture turned green within 2 h. 4-Methylbiphenyl was the sole product (48% based on cobalt). No precipitate was formed.

Experiments with the other compounds mentioned were carried out without solvent at 10°C with a three molar excess of halide to cobalt compound. Analysis was by GC and GC/MS.

Cobalt-containing products. As in earlier work [2], cobalt was recovered as the triphenylphosphine complex or as such as $CoX_2 \cdot nH_2O$. $[Ph_3P]_3CoCl$ was obtained from reactions with aryl chlorides; it oxidizes in the air to a blue complex from which Ph_3P, Ph_3PO and cobalt halides were isolated. Only in the case of reactions of $[Ph_3P]_3CoCH_3$ with bromobenzene and bromotoluene did crystallisation from cold ethanol yield a green powder. Found: C, 64.5; H, 4.85; Br, 11.8; P, 10. $C_{12}H_{10}BrCoP_2$ calcd.: C, 65.0; H, 4.5; Br, 12.0; P. 9.5%. The composition suggests a

dimeric or polymeric species, i.e. $([Ph_3P]_2CoBr)_n$ with $n \geqslant 2$. Triphenylphosphine and $CoBr_2$ were present in the extract.

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