Journal of Organometallic Chemistry, 285 (1985) 293–303
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

COBALT-CATALYSED CARBONYLATION OF ARYL HALIDES

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(Received September 13th, 1984)

Summary

A novel method for carbonylation of aromatic and heteroatomatic halides is described. The catalytic system consists of a combination of alkylcobalt carbonyl complexes, either preformed or made "in situ", and bases such as alkoxides, NaOH and K_2CO_3 in aliphatic alcohols. Under these conditions new anionic cobalt complexes are formed which are characterized by a very high reactivity towards aromatic halides. The latter undergo the carbonylation reaction with high yield under very mild conditions.

Introduction

Several methods for carbonylation of aryl halides which require rather drastic reaction conditions have been described [1]. Some years ago we reported that $Ni(CO)_4$ could catalyse this type of reaction under 1 atm of CO, provided that aprotic dipolar solvents and a base such as $Ca(OH)_2$ were used [2]. The results suggested that nickel carbonyl anions were involved in the catalytic cycle. Later palladium triphenyl complexes were successfully employed in the synthesis of aromatic carboxylic derivatives, such as esters [3], amides [4], lactones [5] and lactams [6] under mild conditions.

More recently these reactions were carried out under phase transfer conditions [7], and some cobalt-based catalysts have also been employed. The catalyst used in these experiments was essentially $Co(CO)_4^-$, under conditions where radical species could be easily formed either by photostimulation [8] or by chemical reactions [9]. $Co(CO)_4^-$ alone, although very effective with aliphatic halides, is completely unable to catalyze the carbonylation of aromatic halides.

We now report some preliminary results obtained using new cobalt-based catalysts [10].

0022-328X/85/$03.30

Results

The carbonylation of aryl halides (eq. 1) can be conveniently catalysed in alcoholic solution by alkylcobalt carbonyl complexes such as those reported in Table 1.

$$ArX + CO + ROH \xrightarrow[\text{Base}]{ECH_2Co(CO)_4} ArCOOR + HX \qquad (1)$$

(P(CO) 1 atm, T 25°C; $R = CH_3$, C_2H_5, i-C_3H_7)

(E = electron-withdrawing group (see Table 1); for ArX see Table 2)

The presence of an electron-withdrawing group in the alkyl chain gives a reasonable stability to these complexes, so that they can be handled easily under an inert atmosphere at about 0°C. We used these complexes as catalysts in ethereal solution, however, without isolating them.

Alkylcobalt complexes of this kind, although previously reported (see Table 1), have never before been used as catalysts; some of them however have been shown to be intermediates in the carbonylation reactions of the corresponding alkyl halides [13]. Many aromatic and heteroaromatic halides can undergo the carbonylation reaction to give the corresponding acid derivatives (see Table 2). The presence of electron-withdrawing groups on the aromatic ring strongly favours the reaction (entries 4–9).

Reasonably high yields were achieved even with high substrate/catalyst ratios (entries 4, 5, 7). In every case the selectivity towards the carboxylic derivatives was practically complete, the only by-product, the aromatic hydrocarbon, being present in almost undetectable amounts. Complexes I and II proved to be more active catalysts than III, IV and V in the cases in which a comparison was made (entries 1, 2; 4, 7, 8; 13, 17). The reactions were usually carried out at room temperature, but they also proceeded quite well at 0°C, albeit more slowly (entries 11, 12).

Methanol was found to be the best solvent, higher alcohols giving lower conversions (entries 11, 15 and 13, 14). As far as the leaving group is concerned, bromides were much more active than the corresponding chlorides. In fact, only aromatic chlorides strongly activated by electron-withdrawing groups in the appropriate position showed activity (entries 5, 6). On the other hand both chloronaphthalenes and chlorothiophenes proved to be quite good substrates (entries 11–18, 21, 22). Sodium hydroxide potassium carbonate, and sodium alcoholates were employed as

TABLE 1

σ-ALKYLCOBALT CARBONYL COMPLEXES OF THE TYPE E–$CH_2Co(CO)_4$ USED AS CATALYSTS

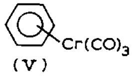
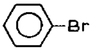
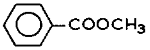
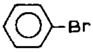
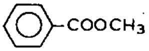
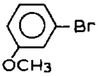
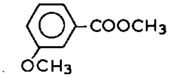
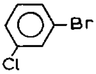
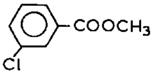
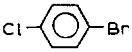
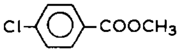
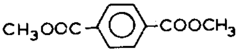
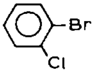
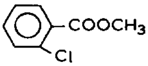
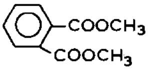
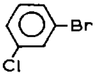
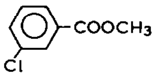
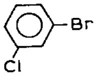
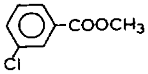
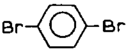
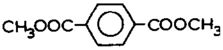
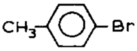
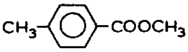
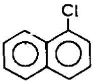
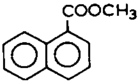
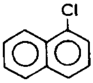
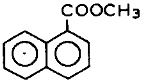
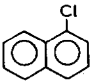
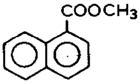
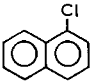
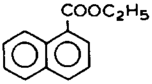
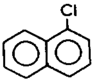
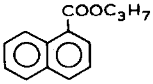
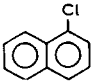
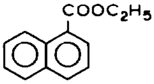
E	ν(CO) (cm^{-1})	Ref.
$COOCH_3$ (I)	2111, 2046, 2036	11
$COOC_2H_5$ (II)	2111, 2046, 2036	11
F (III)	2120, 2048, 2036	12
CN (IV)	2118, 2050, 2036	13
 (V)	2103, 2040, 2023	14

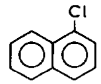
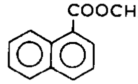
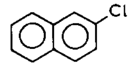
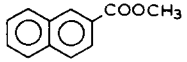
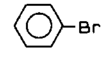
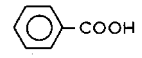
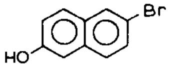
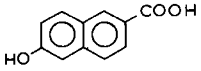
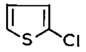
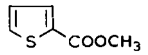
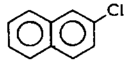
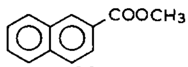
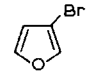
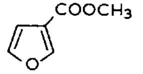
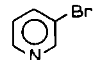
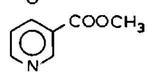
TABLE 2

CARBONYLATION OF AROMATIC HALIDES, ArX, CATALYSED BY $ECH_2Co(CO)_4$ [a]

Entry	ArX	Catalyst	Product (Yield (%))	mol product/ mol Co ratio [b]
1		II	 (86)	30
2		III	 (66)	24
3		II	 (68)	51
4		II	 (78)	216
5		II	 (77)  (1.5)	125
6		II	 (45)  (6.5)	80
7		I	 (76)	161
8		IV	 (43)	82
9		II	 (77)	60
10		II	 (12)	11
11		II	 (67)	30
12 [c]		II	 (16)	30
13		III	 (52)	47
14 [d]		III	 (42)	34
15 [e]		II	 (20)	18
16 [d]		II	 (53)	50

continued

TABLE 2 (continued)

Entry	ArX	Catalyst	Product (Yield (%))	mol product/ mol Co ratio [b]
17		V	 (22)	50
18		II	 (72)	55
19 [f]		II	 (45)	30
20 [f]		II	 (48)	14
21		II	 (78)	65
22 [g]		II	,(33)	21
23		II	 (45).	64
24		II	 (57)	26

[a] Unless otherwise indicated all reactions were carried out at 25°C under atmospheric pressure of CO using ArX (45 mmol), $NaOCH_3$ (45 mmol) in CH_3OH (30–40 ml). [b] This ratio was calculated from the analysis for cobalt and esters at the end of the reactions. [c] T 0°C. [d] Solvent = C_2H_5OH; Base = C_2H_5ONa (45 mmol). [e] Solvent = i-C_3H_7OH; Base = i-C_3H_7ONa (45 mmol). [f] Base = NaOH (120–150 mmol). [g] Base = K_2CO_3 (55 mmol).

bases, the last being the most efficient. The same carbonylations could also be carried out with catalysts generated "in situ" from the reaction between $Co(CO)_4^-$ and an alkyl halide R'X (eq. 2).

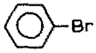
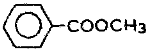
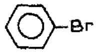
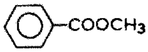
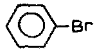
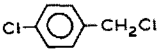
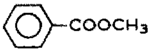
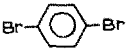
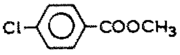
$$ArX + CO + ROH \xrightarrow[Base]{R'X/Co(CO)_4^-} ArCOOR + HX \qquad (2)$$

The results obtained with this catalytic system are listed in Table 3. Low Ar/Co and ArX/R'X ratios were used in this case in order to achieve the highest conversions. The best results were obtained with CH_3I, n-$C_8H_{17}X$, and halides of type ECH_2X where E is an electron-withdrawing group. Benzyl halides were less effective in promoting the carbonylation of aromatic halides, probably because under the conditions used the cobalt-coordinated benzyl groups are easily carbonylated and removed from the complex; the phenylacetic esters formed in this way contaminated the reaction products. When CH_3I or $ClCH_2COOR$ was used, however, alkaline hydrolysis of the product mixture gave acetic or malonic acid, which could be completely removed because of their water-solubility. Finally it is noteworthy that when both aromatic and aliphatic halides are present in the same molecule the presence of an added alkyl halide is no longer required, and the carbonylation of both groups can be catalysed by $Co(CO)_4^-$ alone (entries 16, 17).

The effect of substituents on the phenyl ring has been investigated for both of the

TABLE 3

CARBONYLATION OF AROMATIC HALIDES ArX CATALYSED BY $Co(CO)_4^-$ AND R'X [a]

Entry	ArX	R'X	Product	(Yield (%))
1		n-C_8H_{17}Br		(97)
2		$ClCH_2COOCH_3$		(90)
3 [b]			 [e]	(70)
4		$ClCH_2COOCH_3$		(98)
5		$ClCH_2COOCH_3$		(80)
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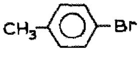
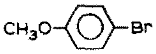
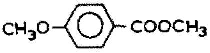
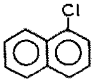
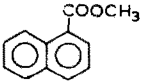
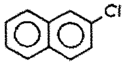
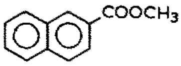
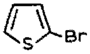
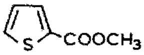
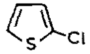
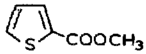
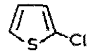
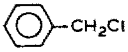
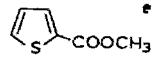
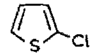
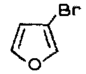
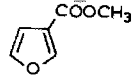
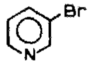
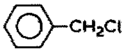
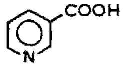
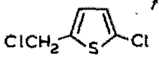
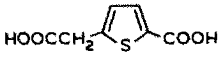
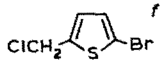
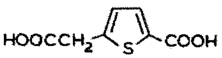
6		$ClCH_2COOCH_3$		(70)
7		$ClCH_2COOCH_3$		(73)
8		$ClCH_2COOCH_3$		(82)
9		$ClCH_2COOCH_3$		(91)
10		$ClCH_2COOCH_3$		(95)
11		$ClCH_2COOCH_3$		(98)
12 [b]			 [e]	(72)
13 [b]		CH_3I		(60)
14		$ClCH_2COOCH_3$		(93)
15 [c]			 [e]	(55)
16 [d]	 [f]	—		(33)
17 [d]	 [f]	—		(50)

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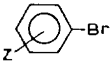
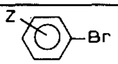
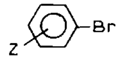
[a] Unless otherwise indicated all reactions were carried out at 60°C under atmospheric pressure of CO using ArX (30 mmol), K_2CO_3 (40 mmol) in CH_3OH (25 ml). ArX/R'X and ArX/Co ratios were 8–9 and 20–30 respectively. [b] T 35°C. [c] T 35°C; Base = NaOH (75 mmol). [d] Solvent = CH_3OH/H_2O (97/3); Base = $Ca(OH)_2$ (45 mmol); T 20–30°C. [e] Phenylacetic acid derivatives were also present in the product mixture. [f] See ref. 17.

TABLE 4

RELATIVE RATES OF CARBONYLATION OF SOME SUBSTITUTED PHENYL BROMIDES

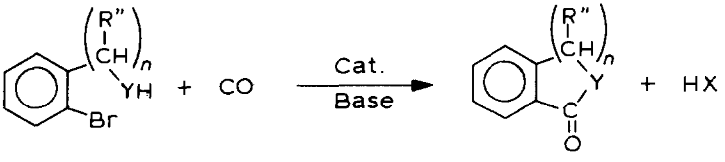


Z	σ	log K/K_0 (Method A) [a]	log K/K_0 (Method B) [b]
p-OCH_3	−0.268	−0.28	−0.23
p-CH_3	−0.17	−0.19	−0.20
H	0	0	0
m-OCH_3	0.115	0.36	0.36
p-Cl	0.227	0.56	0.60
m-Cl	0.373	0.64	0.70
p-CF_3	0.54	0.72	0.77

[a] Method A = Complex II (4×10^{-1} mmol), $NaOCH_3$ (15 mmol),  and C_6H_5Br (10 mmol each) in CH_3OH (20 ml) at 25°C. [b] Method B = $Co_2(CO)_8$ (1.3 mmol); $ClCH_2COOC_2H_5$ (4 mmol); K_2CO_3 (37 mmol);  and C_6H_5Br (15 mmol each) in CH_3OH (25 ml) at 60°C.

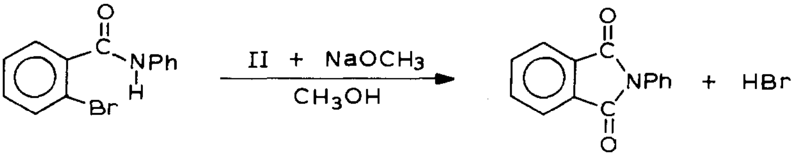
catalytic systems by carrying out competitive reactions (see Experimental). The results of such a study, given in Table 4, show that electron-withdrawing groups strongly increase the reaction rate and electron-releasing groups decrease it; very similar results were obtained with the two catalytic systems, suggesting that the same mechanism operates in both cases and that the two systems are thus equivalent.

The carbonylation reaction has been successfully extended to the synthesis of cyclic compounds such as benzolactones and benzolactams (eq. 3), as already reported for other catalytic systems [5,6,8b]. In this case, also, the carbonylation reaction could be conveniently catalyzed by an alkylcobalt carbonyl, either preformed or made "in situ", and some results are listed in Table 5. The reaction gave γ or δ benzolactones bearing substituents on both aromatic and aliphatic carbons (entries 2–6). For the synthesis of benzolactams, the starting amine can be either primary or secondary, best results being obtained with N-phenyl-o-bromobenzyl amine (entries 13–15). Under carefully chosen reaction conditions synthesis of phthalimides, previously unreported, was also achieved (eq. 4):



(3)

(Y = O, NR"; n = 1,2; R" = H, alkyl, C_6H_5)

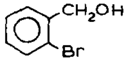
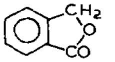
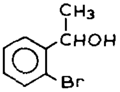
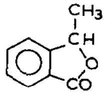
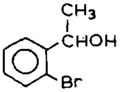
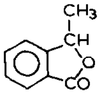
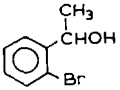
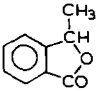
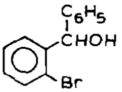
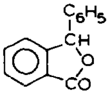
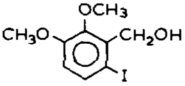
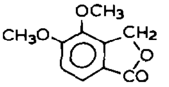
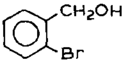
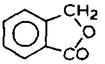
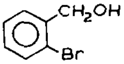
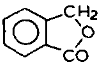
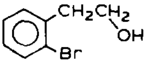
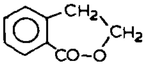
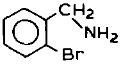
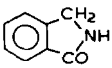
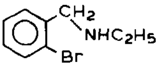
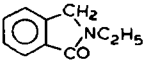
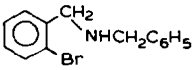
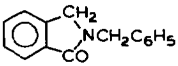
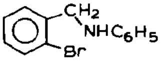
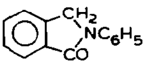
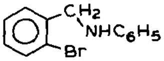
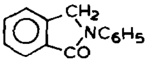


(4)

(P(CO) 1 atm.; T 25°C; mol product/mol Co = 10)

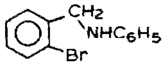
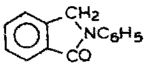
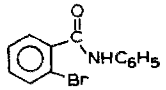
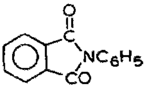
TABLE 5

SYNTHESIS OF CYCLIC COMPOUNDS BY CARBONYLATION OF AROMATIC HALIDES[a]

Entry	Substrate	Base	Product (Yield (%))		mol product/ mol Co ratio
1		K_2CO_3		(70)	16
2	 [18]	$NaOCH_3$		(65)	115
3		NaOH		(60)	36
4		K_2CO_3		(41)	14
5	 [19]	$NaOCH_3$		(42)	10
6	 [5b]	$NaOCH_3$		(77)	72
7[b]		$NaOCH_3$		(77)	10
8[c]		K_2CO_3		(84)	10
9	 [8b]	K_2CO_3		(50)	10
10	 [8b]	$NaOCH_3$		(47)	15
11	 [20]	$NaOCH_3$		(55)	12
12	 [6]	$NaOCH_3$		(62)	18
13	 [21]	$NaOCH_3$		(71)	13
14[d]		$NaOC_2H_5$		(84)	16

continued

TABLE 5 (continued)

Entry	Substrate	Base	Product (Yield (%))		mol product/ mol Co ratio
15[d,e]		$NaOCH_3$		(36)	35
16	 [22]	$NaOCH_3$		(83)	10

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[a] Unless otherwise indicated all reactions were carried out in CH_3OH (30 ml) under atmospheric pressure of CO at 25°C (benzolactones) and 35°C (benzolactams) using complex II as catalyst and ArX (45 mmol); Base = K_2CO_3 (65 mmol), $NaOCH_3$ (50 mmol), NaOH (135 mmol). [b] The catalytic system consisted of $NaCo(CO)_4$ (3.7 mmol) and $ClCH_2COOCH_3$ (6 mmol); the reaction was carried out at 60°C. [c] Catalyst = complex III. [d] Solvent = C_2H_5OH (30 ml). [e] Catalyst = Complex IV.

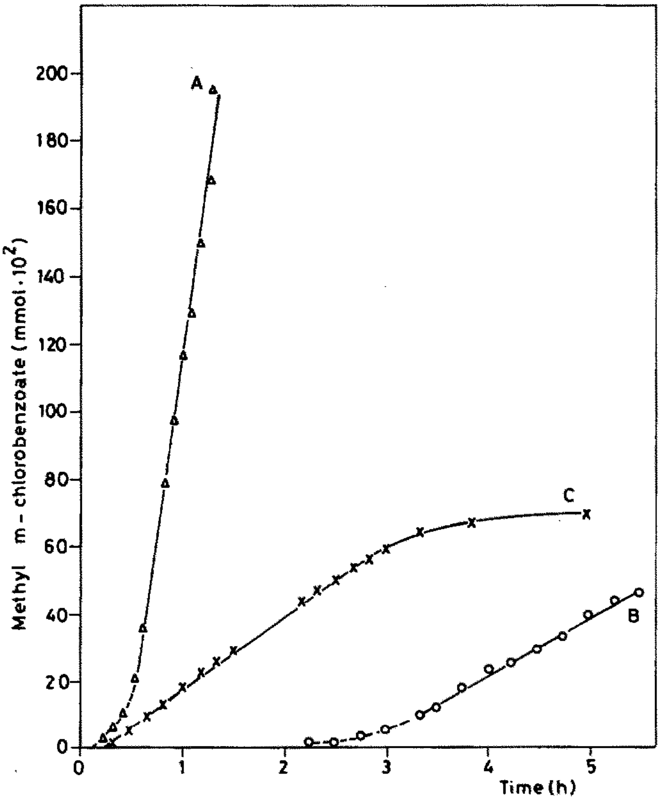


Fig. 1. Initial carbonylation rate of m-ClC_6H_4Br: A, T 15°C; B, T 0°C; C, T 15°C in the presence of styrene (4.3 mmol). Each run was carried out under CO using $NCCH_2Co(CO)_4$ (0.8 mmol), m-ClC_6H_4Br (16.9 mmol), $NaOCH_3$ (2.5 mmol), 1-methylnaphthalene (internal standard) in CH_3OH (20 ml).

Once again complex II was the most effective (entries 1, 8; 14, 15); entries 2–4 clearly show the effect of base strength on the yield, confirming the order of effectiveness as alcoholate > NaOH > K_2CO_3.

Discussion

The reaction mechanism is still far from fully understood, but some features can be noted:

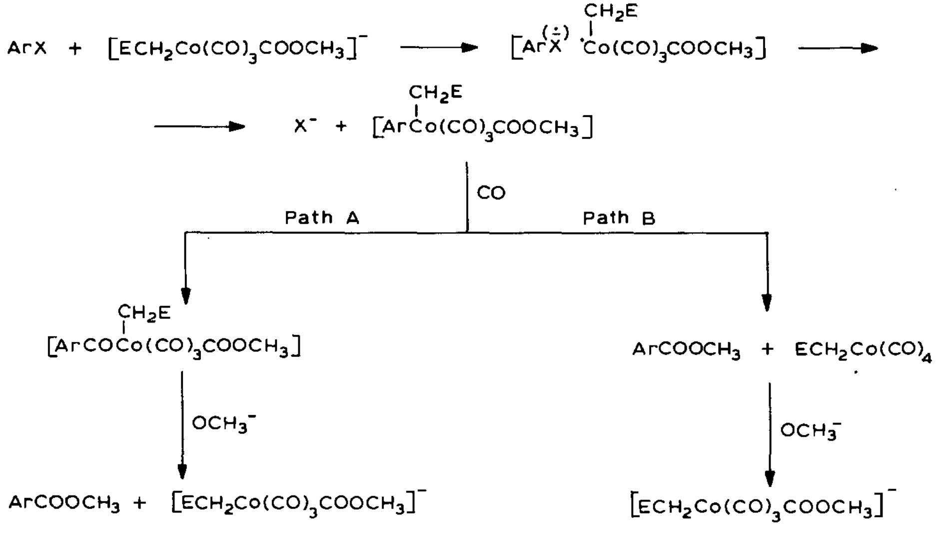
(i) Anionic cobalt complexes of type $[ECH_2Co(CO)_3COOCH_3]^-$ play a role in the catalytic cycle. Thus when the temperature of a methanolic solution of $[NCCH_2Co(CO)_3COOCH_3]^-$ [13] under CO was raised from −40°C to room temperature in the presence of *m*-chlorobromobenzene and sodium methoxide, methyl *m*-chlorobenzoate was formed. Moreover reaction at 16°C in the presence of a less than stoichiometric amount of $NaOCH_3$, stopped when all the base had been consumed. The IR spectrum at this point showed only the characteristic bands of $NCCH_2Co(CO)_4$ [13]. The anionic complex was regenerated and the carbonylation re-started when more base was added.

(ii) The carbonylation reaction showed a temperature-dependent induction time, and was strongly inhibited by the presence of olefins such as styrene (Fig. 1).

(iii) Only very small amounts of hydrogenolysis product were found at the end of the reactions and no coupling products were ever detected.

(iv) The presence of electron-withdrawing groups on the aromatic ring strongly enhanced the reaction rate and yield.

In the light of these observations the following reaction scheme can be proposed (Scheme 1).



SCHEME 1

A substitution of aromatic halides promoted by anionic complexes of Co^I via electron transfer has recently been reported [15]. This kind of process implies that radical species are involved in the reaction. We think, however, that a true S_{RN} mechanism is unlikely, since the presence of free aryl radicals in alcoholic solvents should result in the formation of considerable amounts of hydrogenolysis products; the radical intermediates formed must therefore exist only within a solvent cage as radical pairs. The final product (e.g. the methyl ester) could be formed either by reductive elimination (path B in Scheme 1) or through an acyl complex (path A) formed by migration of the aromatic group onto a carbonyl group bonded to the transition metal atom [16].

Work is still in progress, and further applications of these catalytic systems will be described in future publications.

Experimental

Unless otherwise indicated the aromatic halides and the products were commercially available. Other compounds were prepared by published methods (see Tables).

The products were identified by spectroscopic methods and by comparison with known compounds. The alkylcobalt carbonyl complexes were obtained by published methods (see Table 1). ^1H NMR spectra were recorded with a Bruker WH 90 MHz instrument, GLC/MS spectra with a Varian-Hat CH5-DF spectrometer, and IR spectra on a Perkin–Elmer 983 spectrophotometer.

General procedure for carbonylations catalysed by $ECH_2Co(CO)_4$ (Tables 2 and 5)

The organic solvent (30–40 ml), the aromatic halide (45 mmol) and the base (45–150 mmol) were placed under CO in a flask equipped with a magnetic stirrer, thermometer, and dropping funnel, and a condenser connected to the CO burette. A solution of the catalyst in diethyl ether (5 ml) at −10°C was added during 1–2 h to the reaction mixture kept at 25–35°C. Stirring was continued until CO absorption ceased. Esters and benzolactams were isolated by extraction with diethyl ether of the acidified reaction mixture and purified by conventional techniques. Acids and benzolactones were isolated after alkalyne hydrolysis by extraction of unreacted starting materials and acidification.

General procedure for the carbonylation catalysed by $Co_2(CO)_8$ and R'X (Table 3)

The organic solvent (25 ml), $Co_2(CO)_8$ (1 mmol), the aromatic halide (3.4–3.7 mmol) and K_2CO_3 (40 mmol) were placed under CO in the apparatus described above. The mixture was kept at 60°C and stirring was continued until CO absorption stopped. The products were isolated and identified as described above.

General procedure for the determination of relative rates of carbonylation (Table 4)

Method A. CH_3OH (20 ml), $NaOCH_3$ (15 mmol) and the two aromatic halides (10 mmol each) were placed in the carbonylation apparatus. $C_2H_5OOCCH_2Co(CO)_4$ (0.4 mmol) was added to the mixture at 25°C. After 5 min (a shorter time was used for more reactive halides) a sample was taken, acidified with 1 *N* HCl, extracted with diethyl ether, and treated with CH_2N_2. The molar ratio of the two methyl esters was determined by GLC. Under these conditions no more than 10% of the two halides reacted.

Method B. CH_3OH (25 ml), K_2CO_3 (37 mmol) and $Co_2(CO)_8$ (1.3 mmol) were placed in the carbonylation apparatus. The mixture was kept at 60°C for 15 min, then the two aromatic halides (13 mmol each) and $ClCH_2COOCH_3$ (4 mmol) were added. After 15 min (a shorter time was used for more reactive halides) a sample was taken and worked up as described above.

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