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Intermediates of cobalt-catalysed PTC carbonylation of benzyl halides

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

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Abstract

Intermediates of the cobalt carbonyl-catalysed carbonylation of *ortho*-substituted benzyl halides were identified by IR, ^{1}H- and ^{13}C-NMR spectra. The molecular structures of the acyl-type derivatives 2-$MeC_6H_4CH_2C(O)Co(CO)_3PPh_3$ and 2-$PhC_6H_4CH_2C(O)Co(CO)_3PPh_3$ were determined by X-ray crystallography. Structural features of these complexes are discussed.

Keywords: Phase transfer catalysis; Hydroxycarbonylation; Carbonylation; Acylcobalt carbonyls; Alkylcobalt carbonyls; η_3-benzylcobalt carbonyls

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1. Introduction

Phase transfer catalysis (PTC) became a well-established, environmentally friendly (green) method in preparative organic chemistry [1]. The combination of PTC with transition metal molecular catalysts (TM) is one of the most promising potentialities of transition metal chemistry. TM–PTC is characterised by dramatic increase in reaction rates, consequently enables mild conditions, favourable operational costs and high selectivities [2–8].

The highly complicated multiple interactions operative in these techniques, however, make sometimes difficult the chemical and physical fine tuning of these reactions. It is, therefore, of primary interest to gain insight into the mechanisms. These can be substantially different from those of conventional only-TM, or even of the (related) biphasic-TM variants [9–15].

A few years ago we published an easy, cheap and efficient TM–PTC variant of the cobalt-catalysed hydroxycarbonylation of benzyl halides, using poly-(ethylene-glycol)s (PEG) as phase transfer catalysts [16]. The mechanistic studies in course of this work provided a good example of the above arguments, disclosing new (catalytic) loops of the TM–PTC

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system, catalysed by one of the “intermediates”. This prompted us to perform a systematic, structurally controlled study on the intermediates of this reaction. In a recent paper we described the isolation and X-ray structure of some *para*-substituted benzylcobalt derivatives [17]. Here we report on organocobalt complexes obtained from *ortho*-substituted benzyl halides.

2. Experimental

Starting materials were of commercial origin, with the exception of dicobalt octacarbonyl, which was prepared according to a published procedure [18]. All operations were performed by standard Schlenk techniques [19]. Instruments used were as follows: IR: Bruker FT-IR IFS 113 V; ^{1}H- and ^{13}C-NMR: Bruker AMX 400; mass spectra: HP 5890 GC-HP 5890 AMS instrument; X-ray diffraction: Nicolet R 3 m/V four circle diffractometer, Mo K_α radiation (at 298 K); diffractometer measurement device: Siemens SMART CCD area detector system; diffractometer control software, Bruker AXS SMART Vers. 5.054 1997/1998; computing data reduction: Bruker AXS SAINT program Vers. 6.02A; structure solution and refinement: Bruker AXS SHELXTL Vers. 5.10 DOS/WIN95/NT. Atomic scattering factors were taken from SHELXTL and [20,21]. Corrections for anomalous dispersion were made according to [22].

The procedures followed in the preparation of the benzyl- and phenylacetylcobalt complexes were variants of the procedures described in [16,23–25]. Catalytic and model experiments are summarised in Scheme 1.

2.1. Catalytic carbonylations

The procedure described in [16] was followed, with the following parameters: r.t., 1 bar CO, 12 mmol substrate (benzyl halide) (**1**), 1 mmol PEG 400, 12.5 ml *tert*-amyl alcohol (*t*-AmOH), 12.5 ml 15% aqueous NaOH, 0.5 mmol $Co_2(CO)_8$. Carbonylations using 4-methylpentane-2-one (MP) as organic phase were performed similarly, substituting only *t*-AmOH with the ketone solvent.

Carbonylation yields were (corresponding phenylacetic acids (**5**)): 2-$MeC_6H_4CH_2Br$: 22% (TON 6.6), with MP solvent: 64% (TON 19.2); 2-$PhC_6H_4CH_2Br$: 3.1% (TON 0.45), with MP solvent: 5.8% (TON 0.7); *o,o′*-$BrCH_2C_6H_4C_6H_4CH_2Br$: 7.8% (TON 0.9), with MP solvent: 30.5% (TON 3.7). [TON: turnover numbers, calculated per Co atom introduced.] For comparison: $PhCH_2Br$ with *t*-AmOH solvent 65% (TON 24.4) [16]; with MP solvent 10.2% (TON 3.8). Similar procedure using benzene as organic solvent yielded, with 2-$MeC_6H_4CH_2Br$ exclusively the coupling product *o,o′*-dimethyl-1,2-diphenylethane (**6a**) in 48.7% yield. (Table SM7).

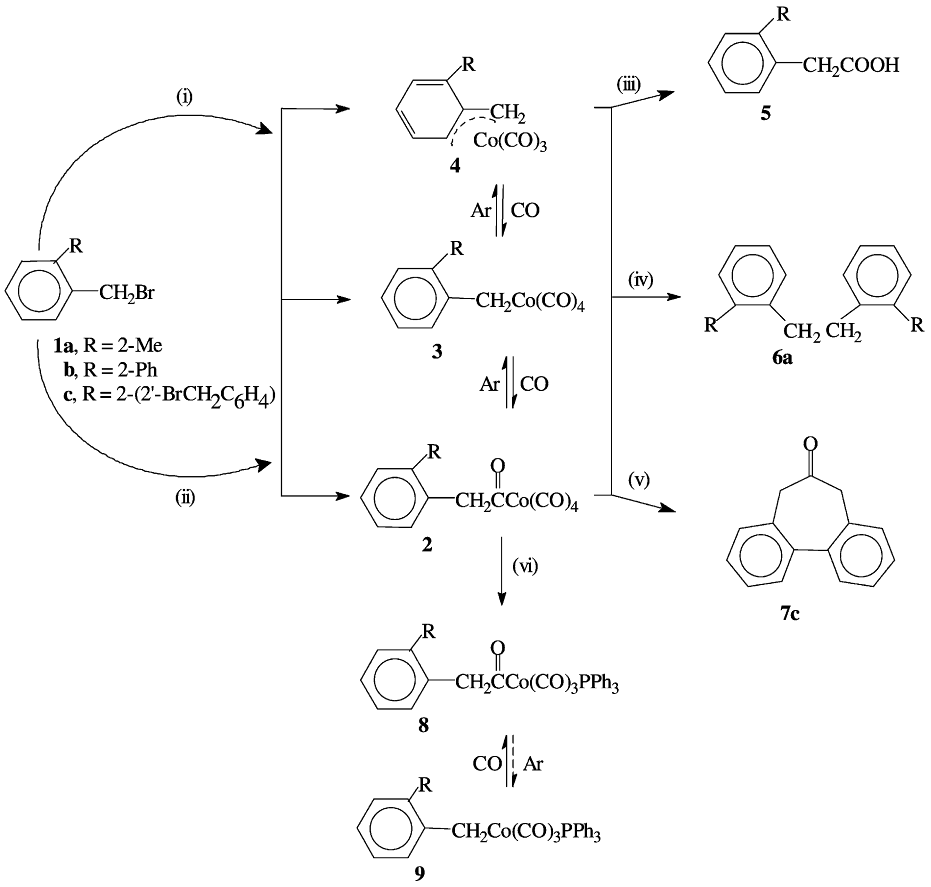
The organic phases of the carbonylation reaction mixtures were analysed time-to-time by infrared spectroscopy and the intermediate cobaltorganic complexes (**2**, **3**, **4**) were identified by model preparations as described in the following part of this paper.

2.2. Preparation of 2-$PhC_6H_4CH_2C(O)Co(CO)_3PPh_3$

$Na[Co(CO)_4]$ (2 mmol) was prepared (with Na/Hg from $Co_2(CO)_8$) in 20 ml of diethyl ether (Et_2O) and cooled to −30 °C. To this solution, under an Ar atmosphere, while being stirred, 2-phenylbenzylbromide (**1b**) (0.48 g [0.36 ml], 2 mmol) was added at once. The reaction mixture, almost immediately became turbid, because of the formation of a white precipitate (NaBr). The reaction mixture was stirred for additional 30 min at −30 °C and then it was left to warm gradually to r.t. and stirring was continued for 1–2 h.

At this point, a sample (0.5 ml) was taken and analysed by IR spectroscopy (2200–1600 cm^{-1} range), which indicated the complete disappearance of the strong, broad band of $[Co(CO)_4]^-$ at ∼1900 cm^{-1}, as well as the evolution of a new band system, which showed the presence of η^3-benzyl$Co(CO)_3$ (**4**) (main product) [9,16,24] and η^1-phenylacetyl$Co(CO)_4$ (**2**) [16,17,23–26] as well as low amount of η^1-benzyl$Co(CO)_4$ (**3**) [16,17,23–26] type complexes together with minor amounts of $Co_2(CO)_8$ and $Co_4(CO)_{12}$ as the only cobalt carbonyl complexes in the solution. The NaBr precipitate was filtered off and the resulting clean brown solution was used for additional experiments.

Treatment of the reaction mixture with CO gas resulted in the increase of the amount of the η^1-phenylacetyl$Co(CO)_4$ type complex as well as



Scheme 1. Preparative experiments: (i) and (iii) PTC (*t*-AmOH or 4-methylpentane-2-one as organic phase); (ii) model experiment with $Na[Co(CO)_4]/Et_2O$; (iv) PTC (benzene as organic phase); (v) thermal decomposition, 0 °C; (vi) PPh_3/Et_2O.

treatment with Ar atmosphere (bubbling through the solution) resulted considerable enrichment of the η^3-derivative. These operations could be repeated, however, no enrichment of the η^1-benzyl$Co(CO)_4$ (alkyl) (**3**) derivative could be achieved, this complex was present always in low concentrations, just on the limit of being observed.

Then, the enrichment of the reaction mixture in the η^1-acyl derivative was achieved by treatment with CO gas. To this solution, while being stirred, under Ar atmosphere at r.t., triphenylphosphine (524 mg, 2 mmol) was added in one portion. The resulting mixture was stirred for 3 h, in course of which a gradual colour change from brown to light yellow was observed. A sample was taken for IR analysis, which indicated the presence of η^1-phenylacetyl$Co(CO)_3PPh_3$ type (**8**) complex [16,17,23–26] as practically the only one cobalt carbonyl species in solution. This product was then obtained in pure form by evaporating the Et_2O solvent and recrystallising the crude product from (layered) Et_2O/*n*-hexane.

The yellow crystalline product (**8b**) (471.7 mg, 41.2 %) was characterised by spectra, elemental analyses (Tables SM4–SM6 and SM9) and X-ray diffraction (Tables SM10–SM17).

An attempt at thermal decarbonylation [26] of $2\text{-}PhC_6H_4CH_2C(O)Co(CO)_3PPh_3$ (**8b**) (Et_2O 32 °C, 8 h, Ar atmosphere), showed a particular stability of this complex, only minor amounts of the alkyl-type derivative $2\text{-}PhC_6H_4CH_2Co(CO)_3PPh_3$ (**9b**) were formed, just enabling spectroscopic detection of this species (Tables SM4–SM6).

Preparation of 2-$MeC_6H_4CH_2C(O)Co(CO)_3PPh_3$ (**8a**) was performed similarly. Spectra, analyses and results of the X-ray structure determination are shown in Tables SM4–SM6, SM9 and SM10–SM17, respectively.

Similar treatment of *o,o′*-$BrCH_2C_6H_4C_6H_4CH_2Br$ (**1c**) resulted very instable η^3-benzyl-, η^1-alkyl and η^1-acyl-type complexes, which decomposed during spectroscopic characterisation as well as during attempts at isolation or substitution by PPh_3. The decomposition yielded a monocarbonylated ring-closure derivative in high yields (81.6%): 3,4;5,6-dibenzocycloheptanone (**7c**) [27], which was characterised by mass as well as ^1H and ^{13}C NMR spectra (Table SM8).

"Model" experiments for the study of the differences in the distribution of intermediates **2**, **3** and **4** under PTC conditions were performed as described above for the preparation of **2b**. The solvent from the final sample was evaporated and the residue was dissolved in *t*-AmOH or MP. These solutions were flushed by Ar or CO gas to achieve decarbonylation/carbonylation reactions. These reactions were followed by IR spectroscopy.

3. Results and discussion

3.1. Preparative results

The preparative results are summarised in Scheme 1.

The TM–PTC hydroxycarbonylation of **1a–c** proceeded with low to medium yields (and TON-s). It is interesting to compare the carbonylation yields obtained with the two solvents (*t*-AmOH versus MP) with the yields observed for unsubstituted $PhCH_2Br$ ([16] and this work) in these solvents, used as organic phases. While for unsubstituted $PhCH_2Br$ *t*-AmOH provides significantly higher yield, than the ketone, substrates **1a**, **1b** and **1c** show higher yields using MP. This "inverted solvent effect" might be attributed to the different distributions of intermediates **2**, **3** and **4**.

Model experiments, carbonylation/decarbonylation of mixtures of complexes **2**, **3** and **4** in these solvents indicate that there are significant differences in these distributions between unsubstituted benzyl- versus *ortho*-substituted benzyl derivatives, as well as for the same derivative in different solvents. This difference can, most probably, be attributed to changes in the relative stabilities, and therefore the distribution of the intermediate cobalt complexes (which in fact was detected, vide infra).

An attempt at using the "classical" organic solvent of TM–PTC carbonylations (benzene) led to only benzyl/benzyl coupling product (**6a**) indicating again the sensitivity of these systems towards all details of the experimental set-up.

The reactions of the in situ generated $[Co(CO)_4]^-$ catalyst precursor were modelled by reactions of $Na[Co(CO)_4]$ (prepared more "cleanly" by Na/Hg in Et_2O). These model reactions yielded a mixture of η^1-acyl$Co(CO)_4$ (**2**), η^1-alkyl$Co(CO)_3$ (**3**) and η^3-benzyl$Co(CO)_3$ (**4**) complexes, as expected on the basis of earlier experience [16,17,23–26], but with some important differences:

(a) only low amounts of alkyl-type complexes **3** were formed (with respect to unsubstituted benzyl derivatives);
(b) the *ortho*-substituted derivatives showed an elevated tendency to form η^3-benzyl$Co(CO)_3$ type complexes (**4**), which enabled also the isolation of **4a** (see [4]);
(c) the cobalt complexes obtained from the disubstituted biphenyl substrate **1c** were unusually instable, starting to decompose already a 0 °C, yielding the interesting C_7-ring derivative **7c**.

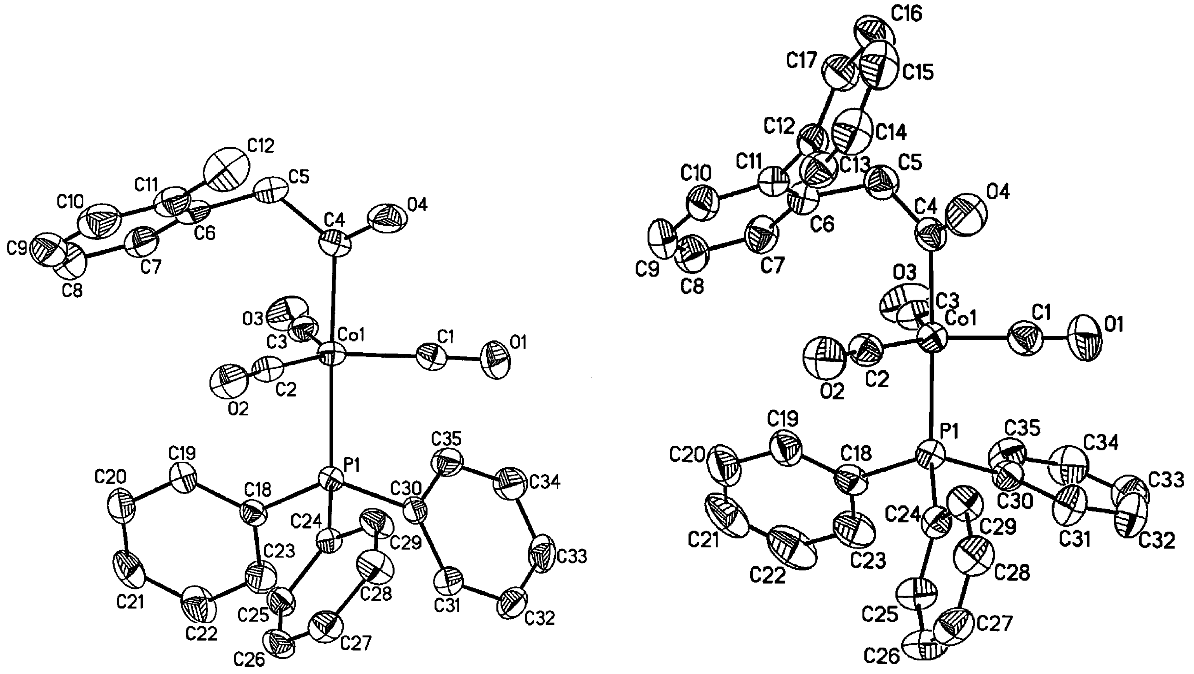
The all-carbonyl complexes were oily substances, which could not be isolated except the η^3-derivative (**4a**) [16].

3.2. Structural results

The η^1-acyl-type complexes **8a** and **8b** could be obtained in crystalline form, the X-ray diffraction structure determination resulted the structures shown in Fig. 1. Experimental details and some structural features are shown in Tables SM10–SM17.

The crystal systems and point groups of the complexes **8a** and **8b** are different, **8a**: monoclinic $P2_1/n$, while **8b**: triclinic $P\bar{1}$ with $Z = 4$ and 2, respectively. Both are centrosymmetric. In spite of these differences the main structural features of the complexes are fairly similar.

The overall geometries are approximately trigonal bipyramidal, with the non-carbonyl ligands in the



8a **8b**

Fig. 1. ORTEP drawing of the molecular structures of complexes **8a** and **8b** (one enantiomer each). Some characteristic parameters are: distances: Co–C(1), Co–C(2), Co–C(3) average 1.792, 1.785; Co–C(4) 2.012(3), 2.031(3); Co–P 2.2642(8), 2.2498(8); C(4)–O(4) 1.202(4), 1.193(4) Å; angles: C(2)–Co–C(3), C(2)–Co–C(1), C(3)–Co–C(1) 117.10–124.32, 114.91–125.80; C(4)–Co–P 177.17(9), 178.12(9); C(5)–C(4)–O(4) 118.7(3), 120.7(3)°, respectively.

two axial positions, as usual in similar complexes [17,24,28–32]. The equatorial carbonyl ligands are deformed because of the steric interactions with the other ligands, as reflected by the non-equivalence of the OC–Co–CO angles. The geometry around the acyl group is "regular".

The organic ligands show a unique orientation: these are turned "side-on" towards the cobalt. This situation appears to be of autosolvation-type interaction [33–37], which is also reflected by the "bending" of the C5, C8 axes (3–5° in both complexes). The two *ortho*-C-s in the aromatic rings are (within 1.7%) equidistant from the Co atom.

The conformations of both complexes show peculiar features:

(i) both *ortho*-substituents show the same orientation with respect to the acyl-O and with respect to the PPh_3 conformation. The ring *si* (enantioface turned towards the Co atom) conformation (in **8a**) is quantitatively correlated to **P** helicity of the phosphine, while the *re*/**P** (in **8b**) correlation in the other complex is only apparent, because of the change in the priority in the corresponding CIP rule;

(ii) in the elementary cell of complex **8a** two pairs of conformational racemates *si*/**P** versus *re*/**M** are present, while in the more restricted cell of **8b** only one pair (*re*/**P** and *si*/**M**).

The particular structural features of the phenylacetyl ligand in these complexes give hints at the reasons for the unusual preference of the η^1-acyl complexes **2a**, **8a**, **2b** and **8b** but still more structural work is necessary to achieve a more detailed interpretation.

The concertedness of the orientations of the enantiofaces of the aromatic ring in the phenylacetyl ligand with the enantiomeric conformations of the PPh_3 ligand provides an important new element to our recent findings with alkylcobalt carbonyl complexes

[38–42]. This correlation clearly shows, how sensitively can "react" an apparently achiral ligand (here the *ortho*-substituted aromatic ring) to chiral informations from an another ligand (PPh_3) mediated by the transition metal.

4. Supporting material

Additional supporting material (SM) is available upon request from the authors. This comprises Tables of IR (SM1, SM4), ^{1}H- and ^{13}C-NMR (SM2, SM3, SM5, SM6) of compounds **2**, **3**, **4**, **8** and **9** as well as ^{1}H-, ^{13}C-NMR and MS of compounds **6a** (SM7) and **7c** (SM8), elemental analyses of compounds **8a** and **8b** (SM9) as well as X-ray diffraction crystal and molecular structure data of compounds **8a** and **8b** (SM10–SM17). The X-ray structure data are deposited in the Cambridge Crystallographic Data Bank under numbers **8a** CCDC 210750 and **8b** CCDC 210751.

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