Intermediates and isomers in the substitution of cobalt carbonyl hydride with tertiary phosphorous ligands

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Mono- and disubstitution of $HCo(CO)_4$ with tertiary phosphines and phosphites was studied by IR and ^1H-NMR spectroscopy. It was found that these substitutions proceed through phosphonium tetracarbonylcobaltate intermediates, leading to a mixture of isomers. The crystal and molecular structure of trans-$HCo(CO)_3[P(O\text{-}p\text{-}C_6H_4Ph)_3]$ was determined by X-ray diffraction.

Keywords: Hydroformylation; cobalt carbonyl/tertiary phosphine system; ^1H-NMR; X-ray diffraction structure

1. Introduction

A major technical application of $HCo(CO)_4$ (1) is the hydroformylation of olefins in the presence of tertiary phosphorous ligands [1–4], PR_3 (R = alkyl, aryl, alkoxy, aryloxy) (2). It is generally assumed that PR_3 derivatives of **1** as $HCo(CO)_3(PR_3)$ (**4**) and $HCo(CO)_2(PR_3)_2$ (**6**) were the actual catalysts in this process. Surprisingly, in spite of the technical importance of this process [3–5], not too much is known about the chemistry of the formation of complexes **4** and **6**. It has been established that the reaction between **1** and **2** is very fast [6] and it is supposed to take a dissociative pathway [7,8]:

$$HCo(CO)_4 \overset{-CO}{\rightleftharpoons} HCo(CO)_3 \xrightarrow{+PR_3} HCo(CO)_3(PR_3)\,.$$

It was our aim to learn more about this problem.

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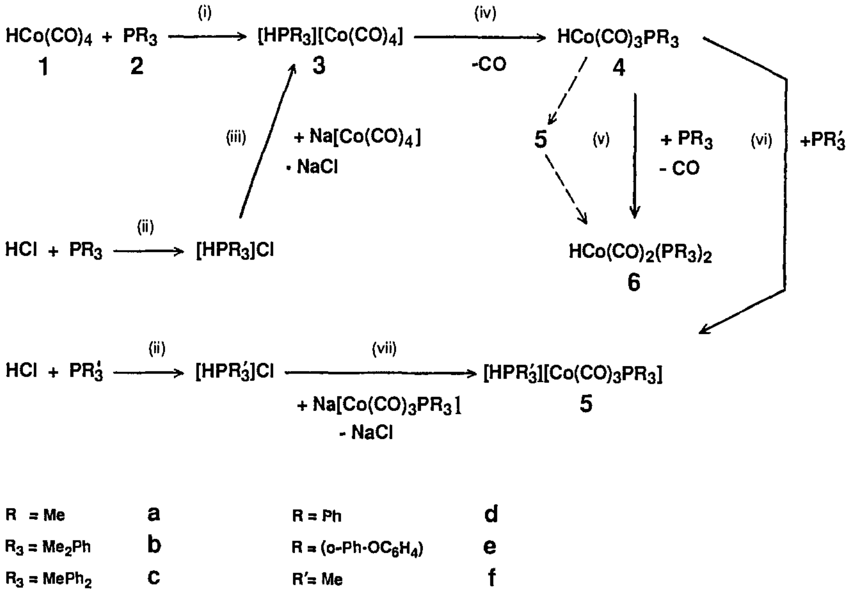
2. Results and discussion

Now we report on preliminary results concerning the intermediates of the formation of mono- and disubstituted derivatives of **1** with ligands **2** and the isomerism of the products.

The preparative results are summarized in scheme 1. (The new compounds were characterized by analyses of some representatives and spectra, as shown in table 1).

Reaction of **1** with a Lewis base **2** at −78°C (reaction (i)) leads to the formation of the corresponding phosphonium tetracarbonylcobaltate (**3**). Slowly warming the reaction mixture results in the gradual formation of the monosubstitution product, $HCo(CO)_3(PR_3)$, **4**. Complexes **4** are formed in two isomeric forms **4A** and **4B**, as a mixture of **4A**+**4B** (minimum of the observed A/B ratio was **4Ac** : **4Bc** ≈ 1 : 1 at −78°C in THF-d_8). Complex **4B** generally isomerizes into **4A** in a fast thermal reaction. These changes can be followed by in situ ^{1}H-NMR measurements (fig. 1). The structures of complexes **3** and **4** were established by



Scheme 1. (i) **1** : **2** = 1 : 1, THF, −78 – −20 °C, 1–30 min. (ii) Excess HCl (g), THF, +25°C, ~ 1 h. (iii) P : Co = 1 : 1, Et_2O, −78 – −20°C, 1–2 h. (iv) THF, −20 – +25°C, 1–120 min. (v) Excess PR_3, THF, +25°C, 1–24 h. (vi) **4** : PR'_3 = 1 : 1, THF, +25°C, 1–10 min. (vii) PR'_3 : Co = 1 : 1, Et_2O, +25°C, 1–2 h.

Table 1
Characteristic spectroscopic data of compounds **3**–**6**

Compound	Spectra, IR (ν(C–O) (cm^{-1})); ^{1}H-NMR (200 MHz, (ppm); TMS)
3a	IR[THF]: 2002vw, 1901s,sh, 1886vs; ^{1}H-NMR(THF-d_8, −40°C): 2.02 [dd, ^2J(PH) = 16.5 cps, ^3J(HH) = 5.3 cps, 9H; $C\underline{H}_3$]; 6.33 [double decet, ^1J(PH) = 510.7 cps, ^3J(HH) = 5.7 cps, 1H; $P\underline{H}$];
4Ac	IR[toluene/*n*-hexane (1 : 1)]: 2050w, 1973vs; ^{1}H-NMR(THF-d_8, −60°C): −10.72 [d, ^1J(PH) = 54.9 cps, 1H; $Co\underline{H}$]; 2.22 [d, ^2J(PH) = 9.0 cps, 3H; $C\underline{H}_3$] 7.4 [m, 10H ar-$C\underline{H}$];
4Bc	^{1}H-NMR(THF-d_8, −60°C): −10.87 [d, ^2J(PH) = 48.5 cps, 1H, $Co\underline{H}$]; 2.2 [d, ^2J(PH) = 9.0 cps, 3H, $C\underline{H}_3$] 7.4 [m, 10H, ar-$C\underline{H}$];
5ad	IR[Et_2O] 1973vs, 1908vs, 1884m; ^{1}H-NMR(THF-d_8, +25°C): 1.56 [d, ^2J(PH) = 10.2 cps, 9H, $C\underline{H}_3$] 7.26 [m, 15H, ar-$C\underline{H}$] ~ 5.8 [dm, partly covered by the Me band, ^1J(PH) =~ 510 cps, ~ 1H, PH];
6Aa	IR[toluene/*n*-hexane (1 : 1)]: 1951vs, 1896vs; ^{1}H-NMR(THF-d_8, +25°C) −11.8 [asymm. virtual t, ^2J(PH) = 17.6 cps, 1H; $Co\underline{H}$]; 1.3 [d, ^2J(PH)= 8.0 cps, 18H, $C\underline{H}_3$]
6Bc	IR[toluene/*n*-hexane (1 : 1)]: 1979vs, 1919vs; ^{1}H-NMR(THF-d_8, +25°C) −11.4 [t, ^2J(PH) = 19.5 cps, 1H, $Co\underline{H}$]; 1.42 [d, ^2J(PH)=4.0 cps, 3H, $C\underline{H}_3$]; 7.24 [m, 10H, ar-$C\underline{H}$].

pounds[#1] and the X-ray diffraction structure determination of a representative of the type **4A** (**4Ae**, fig. 2). This is the first X-ray structure of a monosubstituted phosphite derivative of $HCo(CO)_4$[#2]. These data identify complexes **4A** as being of trigonal bipyramidal geometry with trans-axial H and ligands **2**, complexes **4B** as the corresponding cis-isomers.

The Brønsted acidity of the hydrides **1** and **4** as well as the basicity of the ligands **2** play an important role in these transformations. Hydride **1** is a strong acid [21], consequently its phosphonium salts **3** are relatively stable. However, the stability of these salts is sensitive to the basicity of **2**, as characterized by the **3** → **4** transformation (reaction (iv)) temperatures: **2a** (25°C, ~ 30 min), **2b** (−10°C, ~ 30 min),

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[#1] For $[R_3NH][Co(CO)_4]$ derivatives see refs. [9–11]. For tertiary phosphonium salts ref. [12]. For trans-$RCo(CO)_3L$ complexes see e.g. refs. [13–15], for cis-$RCo(CO)_3L$ ref.[16].

[#2] The closest analog, $HCo(CO)_3[c\text{-}Hex)_3]$, ref.[17]. Other simular structures include trans-$HCo(CO)(PPh_3)_3$, ref.[18]; Co–H=150 pm. trans-$HCo(N_2)PPh_3)_3$, ref.[19]. $HCo(PEt_3)_4$, ref.[20]; Co–H=138 pm.

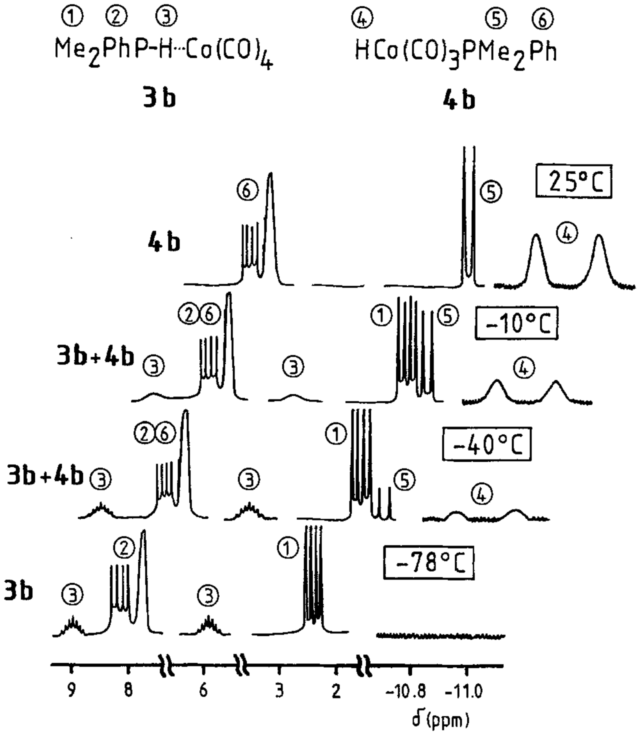


Fig. 1. ^1H-NMR investigation of the reaction of PMe_2Ph (**2b**) with **1** in THF-d_8 between −78 and 25°C.

2c (−40°C, ~ 20 min), while at **2d** the transformation is so fast that **3d** could not be observed spectroscopically even at −78°C. The substituted hydrides **4** are much weaker acids and their acidity is expected to decrease with increasing basicity of the coordinated ligand **2** [22]. Consequently salts **5** are extremely instable. These complexes could be clearly observed only with combinations where the "first" ligand **2** is much less basic than the "second" one, as $PR_3 = PPh_3$ and $PR'_3 = PMe_3$ (**5ad**). (The mechanism of the "second" substitution, scheme 1, **4**→**5**→**6**, was deduced on this basis.)

The intermediacy of complexes **3** and **5** in transformations **1**→**4** and **4**→**6** respectively, was also supported by alternative syntheses (iii) and (vii).

The structure of complexes **5** and **6** was based on analyses, IR ν(CO) and ^1H-NMR spectra and analogies of the latter [23]. Complexes **6** are often formed in two isomeric forms (scheme 2). The more stable configuration, **6A**, appears to be of trigonal bipyramidal structure, with (mer-) axial H and equatorial and axial **2**, while to the less stable isomer, **6B**, a tetragonal pyramidal structure with axial H and trans-PR_3 ligands can be (tentatively) assigned on the basis of the spectroscopic data [23]. The relative stability of **6A** and **6B** depends on the nature [22] of the ligand **2**.

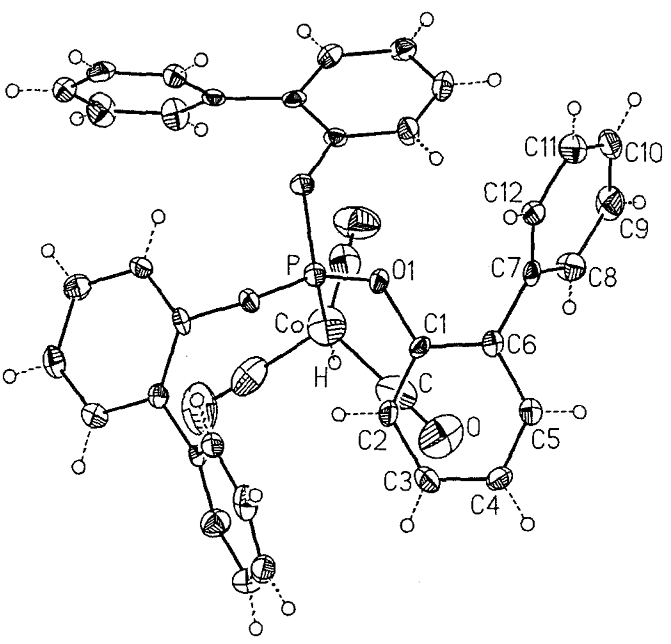


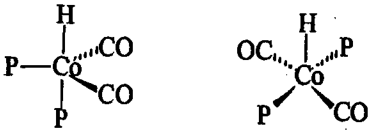
Fig. 2. Molecular structure of $HCo(CO)_3[P(o\text{-}Ph\text{-}OC_6H_4)_3]$ (4e). Selected interatomic distances (pm): Co–H 149.7(5), Co–P 221.6(3), Co–C (01), Co–C (01B) 177.9(6); angles (deg.): H–Co–P 180(1); P–Co–C(01) 113.7(2); Co–C(01)–O(01) 178.1(5).

Spectroscopic and ligand effect arguments as well as X-ray and neutron diffraction structures of the analogous ammonium salts $[R_3NH][Co(CO)_4]$ (R = Me, Et) [9,11] identify complexes **3** and **5** as ion pairs associated by a kind of H-bridge. This fact compared with the more easy substitution of the $[Co(CO)_4]^-$ anion in these complexes (cf. scheme 1 and ref. [6]) than in tetracarbonylcobaltates associated with metal cations (Li^+, Na^+, K^+, Tl^+) [24–26] indicates that the E–H...C(O)–Co (E = N, P) type association [9] is apparently more efficient in the activation of $[Co(CO)_4]^-$, than the M...O–C–Co type [26,27].

3. Conclusions

The results of this study should be considered in the interpretation of the initial steps of the cobalt catalyzed hydroformylation [3–5]. A logical extension of the results would be to suppose protonation as the very first step of the interaction of the cobalt hydride with the olefin, preceding the formation of the hypothetic "olefin complexes":

$$\text{olefin} + HCoL_x \rightleftharpoons [\text{olefin} \cdot H]^+[CoL_x]^- \rightleftharpoons HCo(\text{olefin})L_{x-1} + L$$
$$(L = CO, PR_3)$$



6A **6B**

Scheme 2.

$$\text{olefin} + \mathrm{HCoL}_x \rightleftharpoons [\text{olefin}\cdot\mathrm{H}]^+[\mathrm{CoL}_x]^- \rightleftharpoons \mathrm{HCo(olefin)L}_{x-1} + \mathrm{L}$$
$$(\mathrm{L} = \mathrm{CO}, \mathrm{PR}_3)$$

A similar initial mechanism appears to be quite generally probable at the hydride transfer from metal to organic substrates [28]. The easy conversion of isomers **4B** into **4A** is the first experimental indication of the possibility, that (supposed) primary cis-$RCo(CO)_3(PR_3)$ or cis-$RC(O)Co(CO)_3(PR_3)$ compounds (required by the theory of "migratory insertion"[29]) could isomerize into the corresponding trans-isomers, de facto observed [13,15,30] after decarbonylation and/or carbonylation respectively. (No sign of eventual formylcobalt intermediates was observed when the formation of complexes **4** and **6** was followed by low temperature ^{1}H-NMR.)

4. Experimental

The standard Schlenk inert technique was used. $HCo(CO)_4$ was prepared according to published procedures [31].

The ^{1}H-NMR measurements were performed by BS-487C (80 MHz, Tesla), Bruker AMX-400T and Varian XL-200T instruments. Samples for NMR spectroscopy were filled under deoxygenated Ar atmosphere.

X-ray determination of **4e**. Crystal dimensions: 0.26 × 0.21 × 0.18 mm^3. Nicolet R3m/V diffractometer, Mo Kα radiation at 110 K. Cell dimensions (from the diffractometer angles of 25 centered reflections) $a = b = c = 18.496(2)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 6329.2(1.5)$ Å^3; $Z = 6$, $d_{\text{cal}} = 1.068$ g cm^{-3}, $u = 0.47$ mm^{-1}, cubic space group Pa3 (no. 205), data collection of 3629 intensities, 1546 unique ($R_{\text{merg}} = 0.021$), $2\Theta_{\max} = 50°$, 743 observed ($F_0 \geqslant 4\sigma(F)$), structure solution with direct methods and refinement with full matrix least squares, 145 parameters, rigid groups applied for H atom positions and common isotopic U-values ($U = 0.020$ Å^2) except the Co-bonded H atom which was refined with a Co–H distance constraint to 1.5 Å ($U = 0.029$ Å^2); anisotopic ADPs for all other atoms. $R = 0.038$, $R_w = 0.036$, $w^{-1} = (\sigma^2(F_0) + 0.001\ F_0^2)$. Maximum residual electron density 0.63 e Å^{-3}. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Energie, Physik, Mathematik

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