Concerted Development of Chiral Conformations in [(Alkyloxycarbonyl)methyl]tricarbonyl(triphenylphosphane)cobalt Complexes

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The *trans*-[(alkyloxycarbonyl)methyl]tricarbonyl(triphenylphosphane)cobalt complexes $[ROC(O)CH_2]Co(CO)_3PPh_3$ (R = Me, *n*Pr, *i*Pr, *t*Bu, and *c*Hex) have been prepared and characterized by IR, ^1H, ^{13}C, and ^{31}P NMR spectroscopy. Crystal and molecular structure determination by X-ray diffraction analysis revealed the following phases: $P\bar{1}$ (R = Me), $P2_1/n$ (R = *n*Pr), $P\bar{1}$ (R = *i*Pr), $P2_1/c$ (R = *t*Bu), $P\bar{1}$ and $P2_1/c$ (R = *c*Hex). The results show concerted development of chiral conformations (both enantiomers) in all cases.

Introduction

The generation of molecular chirality presents an attractive challenge, both from an intellectual and a preparative point of view.[1] The mechanisms for the transfer of chiral information from one reacting group or molecule to the product are of the utmost importance for the design of more efficient systems.[2] In transition metal catalysed or assisted reactions, this transfer is usually an intramolecular process.[3] Since a number of the most efficient chiral ligands used in asymmetric catalysis (e.g., BINAP) exhibit conformational chirality,[4] the development of chiral conformations[5] in transition metal complexes acting as catalysts in these reactions represents an important research goal.

As part of a program aimed at learning more about the mechanisms of intramolecular transfer of chiral information in mono-[6] and dinuclear[7] organocobalt complexes, we have undertaken a systematic preparative and structural study of the [(alkyloxycarbonyl)methyl]tricarbonyl(triphenylphosphane)cobalt complexes, $[ROC(O)CH_2]Co(CO)_3PPh_3$ (R = Me, *n*Pr, *i*Pr, *t*Bu, and *c*Hex).[8] The results obtained with these complexes are reported herein.

Results and Discussion

trans-[(Alkyloxycarbonyl)methyl]tricarbonyl(triphenylphosphane)cobalt complexes (**3**) with achiral alkyl groups in the ester fragment (Me: **a**; *n*Pr: **b**; *i*Pr: **c**; *t*Bu: **d**; *c*Hex: **e**) were prepared in three steps. These steps (Scheme 1) consisted of ion metathesis, ligand-promoted carbonylation, and subsequent thermal decarbonylation.

$$\underset{\mathbf{1}}{ROC(O)CH_2Co(CO)_4} \xrightarrow[PPh_3]{Et_2O,\ r.t.} \underset{\mathbf{2}}{ROC(O)CH_2C(O)Co(CO)_3PPh_3}$$

$$\underset{\mathbf{2}}{ROC(O)CH_2C(O)Co(CO)_3PPh_3} \xrightarrow{\Delta T} \underset{\mathbf{3}}{ROC(O)CH_2Co(CO)_3PPh_3} + CO\uparrow$$

R = Me (**a**), *n*Pr (**b**), *i*Pr (**c**), *t*Bu (**d**), *c*Hex (**e**)

Scheme 1

The constitutions and structures of complexes **3** were established by elemental analyses, by IR and NMR spectroscopy (spectroscopic data were compared with those of previously characterized compounds of similar structure[6b,6c,8–10]), and by determination of the crystal and molecular structures of the crystalline products by X-ray diffraction analysis (Figures 1–3; Tables 1–6 in the Exp. Sect.).

The crystal structures belong to centrosymmetric space groups with two or four molecules per unit cell, respectively. The *c*Hex ester complex **3e** was obtained in two different crystal forms ($P\bar{1}$ and $P2_1/c$ phases), highlighting the fact that the conformational effects are not critically dependent on intermolecular forces but rather on intramolecular interactions. Complex **3a** contains one diethyl ether solvate

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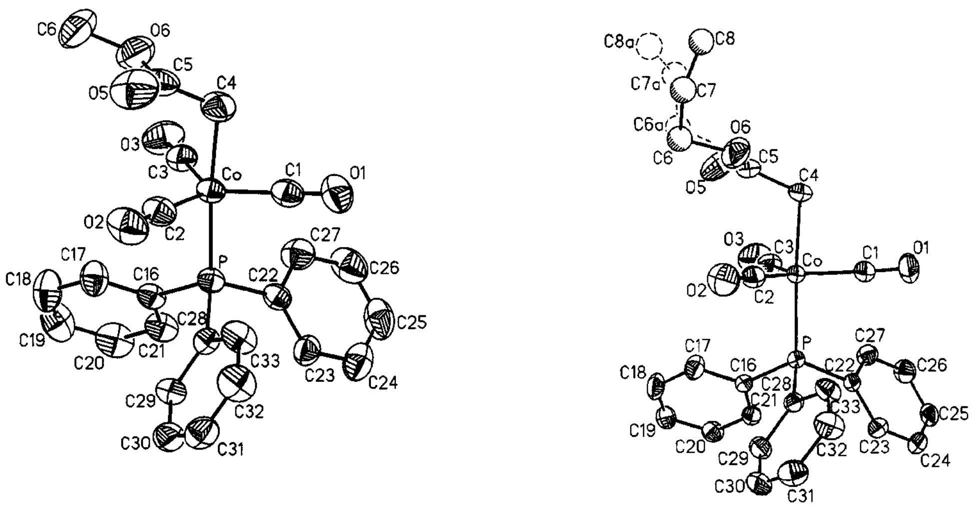
molecule for every two molecules of the complex in the lattice of the $P\bar{1}$ phase; crystalline phases of the complexes **3b**−**e** were found to be solvate-free.

The X-ray diffraction results show that the overall molecular structure of complexes **3** (Figures 1−3) can be described in terms of approximate trigonal-bipyramidal geometry, with the two non-carbonyl ligands in the axial positions, which is a common feature of all alkyl-type [RCo(CO)$_3$L][6b,6c,8a,9b,9c,11,12] and acyl-type [RC(O)Co(CO)$_3$L] (L = tertiary phosphane, I$^-$)[9b,9c,12,13] monosubstituted carbonylcobalt complexes. The molecules of complexes **3** may be regarded as being composed of three main moieties: (i) the (alkyloxycarbonyl)methyl fragment, (ii) the central (equatorial) Co(CO)$_3$ group, and (iii) the triphenylphosphane ligand (Scheme 2).

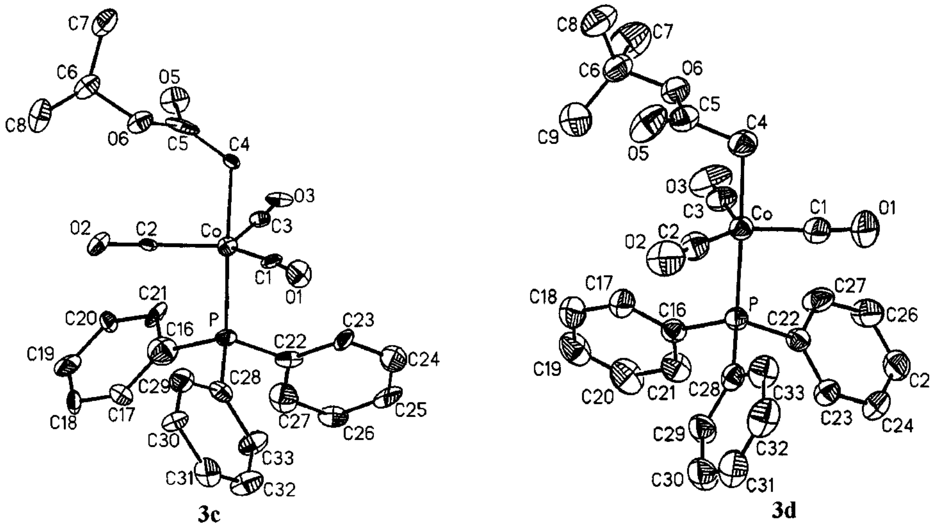
These moieties are linked by two single bonds, Co−C(H$_2$) and Co−P, about which rotation can occur. The C(H$_2$)−C(O) and P−C$_{ar}$ bonds, rotations about which are directly related to the chiral inversions, are far away from each other with the cobalt atom and the Co−C(H$_2$) and Co−P bonds in between. The plane of the five heavy atoms of the ester group C−C(O)OC is oriented quasi-parallel to the plane of the Co(CO)$_3$ group (interplanar angle less than 25°). Other possible conformations of this group allowed by the rotation around the $C_{sp}{}^2-C_{sp}{}^3$ bond are not populated. The slightly bent carbonylcobalt "plane" (consisting of seven atoms) has its concave face directed towards the ester fragment.

The σ-bond system that extends along the molecular axis is composed of two- and threefold conformational axes and adopts a highly relaxed staggered conformation throughout the molecule. The substituents at the sp^3-carbon atom (adjacent to Co), i.e. two H atoms and the ester group, are positioned above the OC−Co−CO forks (Scheme 3).



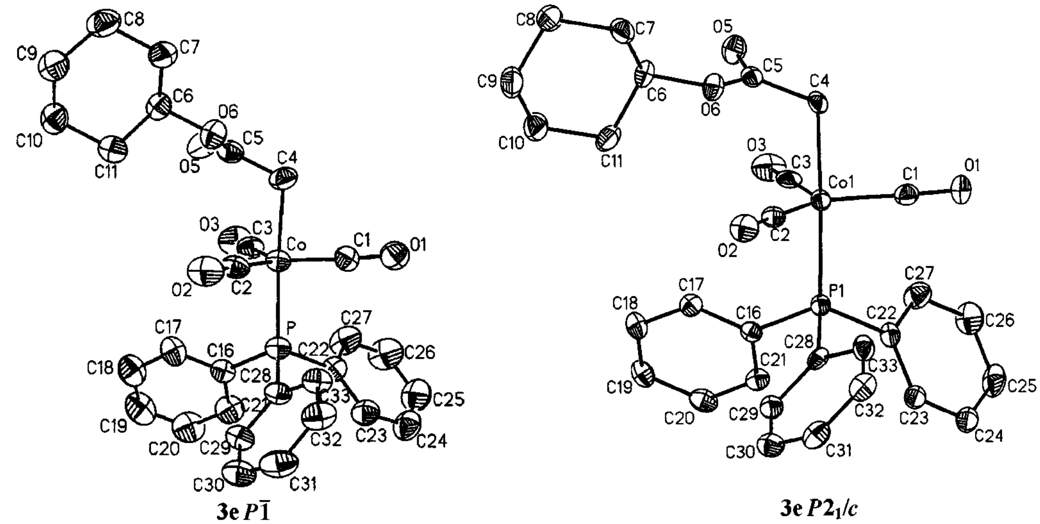
3a **3b**

Figure 1. ORTEP drawing of the X-ray molecular structure of the complexes **3a** and **3b**, perpendicular view to the Co−P axis (one structure each)



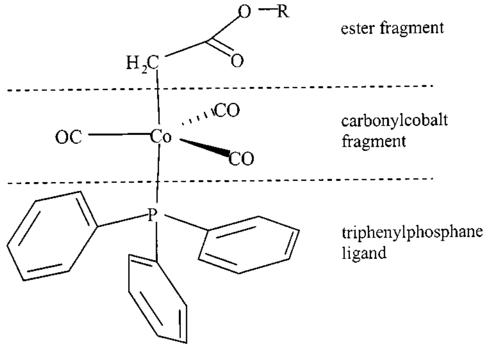
3c **3d**

Figure 2. ORTEP drawing of the X-ray molecular structure of complexes **3c** and **3d**, perpendicular view to the Co−P axis (one structure each)

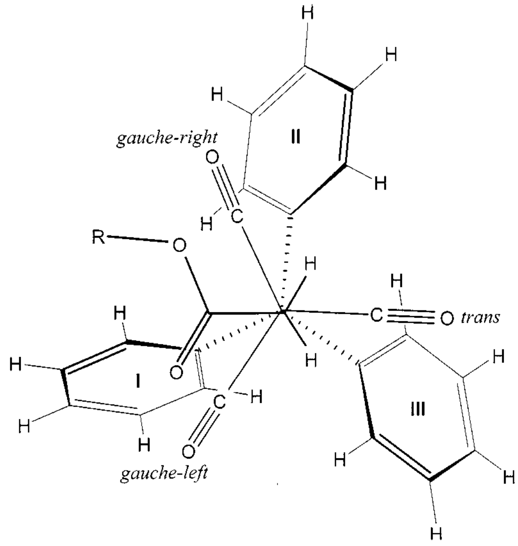


3e $P\bar{1}$ **3e** $P2_1/c$

Figure 3. ORTEP alrawing of the X-ray molecular structure of complex **3a** ($P\bar{1}$ and $P2_1/c$ phases), perpendicular view to the Co−P axis (one structure each)



Scheme 2. Main fragments of the complexes **3**

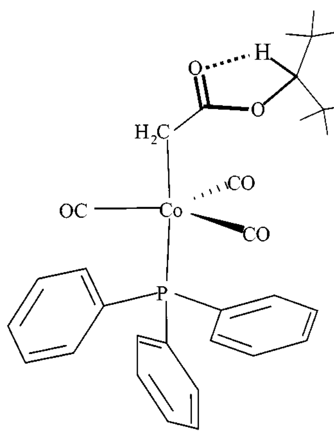


Scheme 3. Complexes **3**, view in the Co−P axis

Due to the bulkiness of the ester group, the adjacent OC−Co−CO angle is widened to release the strain, with a concomitant compression of the other angles at Co. The staggered conformation of the $Co(CO)_3-PPh_3$ rotor is manifested in the orientation of the *ortho*-H atoms of the aromatic rings towards the equatorial plane rather than in the orientations of the $P-C_{ar}$ bonds. The "natural" (as in the free ligand) propeller shape of the triphenylphosphane ligand is preserved, but the positions ($Co-P-C_{ar}-C_{ar}$ angles) of the individual phenyl rings are not identical in complexes **3a**−**e** due to the perturbation, which seems to be most pronounced at the Ph group denoted by **I** in Scheme 3. This perturbation is clearly less pronounced in the methyl ester (**3a**) and the *n*-propyl ester (**3b**) and reaches a maximum in the isopropyl derivative (**3c**). It is not so great in the *tert*-butyl ester (**3d**), for reasons which will be discussed later.

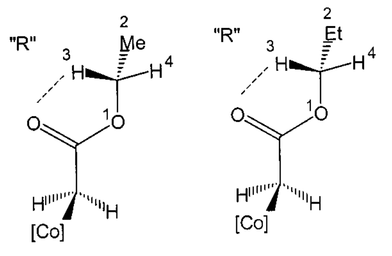
An interesting feature seen in all but one (**d**) of the complexes **3** is a relatively short intramolecular contact between an α-H atom of the ester group and the ester carbonyl oxygen atom, as illustrated for the cyclohexyl derivative **3e** in Figure 4. The distance of this intramolecular interaction is certainly within the limits for H-bonding[14,15] (2.9−3.3[14a] or even 3.6 Å[14b] between two bridged heavy atoms). The five atoms (O−C−O−C−H) define a somewhat distorted ring. The formation of such a ring cannot be observed in the case of the *t*Bu derivative (**3d**), which lacks an α-H atom on the ester group. The charge transfer to the ester carbonyl group is also reflected in a shift to higher wavenumbers of its ν(C−O) band in the solution IR spectra; complex **3d** shows the lowest-energy absorption in this series. This systematic change in the solution spectra also indicates that the ring-forming H-bond interaction remains intact in *n*-hexane solution. The formation of this H-bonded ring obviously contributes to the rigidity of the ester group.

Where the ester has two α-H atoms, the >C=O···H−C(H)R interaction leads to a differentiation of the hydrogen atoms of this $>CH_2$ group. This generates a centre of chirality at the ester α-$C_{sp}{}^3$ atom of complex **3b** as well as at the corresponding position in the Et derivative



	OH (Å)	O-C(sp^3) (Å)	O-C-O-C (deg.)	C-O-C-H (deg.)
3e P-1	2.317	2.699	1.0	-21.3
3e $P2_1/c$	2.264	2.703	10.4	-11.0

Figure 4. Conformations of the ester and triphenylphosphane ligands

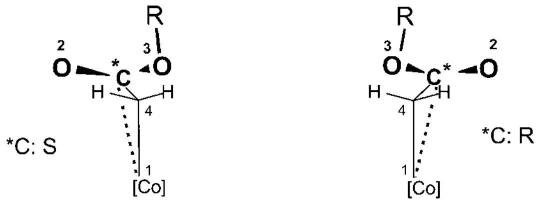


[Co] = *re*,**P**-Co(CO)$_3$PPh$_3$

Scheme 4. New centres of chirality generated by hydrogen bonding

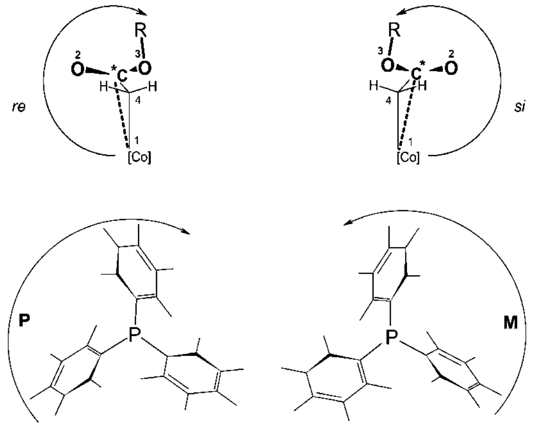
(discussed elsewhere[8a,16]), as shown in Scheme 4. We were, however, unable to detect this effect in the solution phase by low-temperature ^1H NMR spectroscopy down to −80 °C in CD_2Cl_2 or to −50 °C in [D$_6$]acetone.

An additional "through-space" interaction could be identified between the Co atom and the ester $C_{sp}{}^2$ atom in complexes **3a−e**. These atoms are separated by only 292−298 pm (Table 6), which is significantly shorter than the sum of the van der Waals radii (Co−C 385 pm[17]), indicating a kind of coordinative interaction (termed "autosolvation"[18]) between these atoms. As a result of this interaction, the carboxyl $C_{sp}{}^2$ atom becomes tetracoordinated; since it then bears four different substituents, it can adopt (*R*) and (*S*) enantiomeric configurations, as shown in Scheme 5.



Scheme 5

The overall approximate trigonal-bipyramidal geometry of complexes **3** is very important with regard to the main viewpoint of the present study: The *trans*-axial distribution of the (generally) flexible alkyl (or acyl) and phosphane ligands provides an ideal situation for the investigation of concertedness in the development of certain conformations in these ligands on the "opposite" sides of the molecule. In fact, a quantitative concertedness can be observed for the conformations of the ester fragment, with respect to the Co(CO)$_3$ moiety, and the triphenylphosphane ligand in all derivatives **3** described herein (the schematic representation



Scheme 6

Table 1. ν(C−O) bands in the FT-IR spectra of compounds **1−3** in *n*-hexane [cm^{-1}]

	a	b	c	d	e
1	2112 m, 2046 s, 2037 vs, 2028 vs, 1752 vw, 1721 w	2112 m, 2046 s, 2036 vs, 2027 vs, 1746 vw, 1717 w	2111 m, 2046 s, 2036 vs, 2027 vs, 1750 (sh), 1742 w, 1713 m	2111 m, 2044 s, 2035 vs, 2026 vs, 1760 (sh), 1740 m, 1708 w	2111 m, 2045 s, 2035 vs, 2027 vs, 1760 (sh), 1740 w, 1715 w
2	2050 vw, 1986 s, 1975 s, 1755 w, 1702 w	2053 w, 1987 s, 1969 s, 1747 m, 1680 m	2050 vw, 1988 s, 1978 s, 1744 w, 1704 w	–[a]	2046 w, 1984 s, 1975 s, 1740 w, 1700 w
3	2050 vw, 1985 s, 1974 s, 1712 w	2050 vw, 1985 s, 1974 s, 1709 w	2050 vw, 1984 s, 1974 s, 1704 w	2050 vw, 1984 s, 1973 s, 1700 w	2046 w, 1984 s, 1975 s, 1705 w

[a] Decomposed during measurement.

Table 2. ^{1}H NMR signals due to the CH_2 protons in complexes **1** and **3** in $CDCl_3$ (δ in ppm, *J* in Hz)

	a	**b**	**c**	**d**	**e**
1	2.19	2.19	2.19	2.18	2.19
3	2.20 ($^{3}J_{HP} = 3.34$)	2.20 ($^{3}J_{HP} = 2.86$)	2.20 ($^{3}J_{HP} = 2.93$)	2.15 ($^{3}J_{HP} = 2.86$)	2.16 ($^{3}J_{HP} = 3.10$)

Table 3. ^{13}C NMR signals (^{1}H-decoupled) of the CH_2 carbon atoms in complexes **1** and **3** in $CDCl_3$ (δ in ppm, *J* in Hz)

	a	**b**	**c**	**d**	**e**
1	6.98	7.98	8.03	8.04	8.01
3	4.56 ($^{3}J_{CP} = 16.318$)	5.75 ($^{3}J_{CP} = 16.518$)	5.76 ($^{3}J_{CP} = 16.452$)	5.85 ($^{3}J_{CP} = 16.454$)	5.78 ($^{3}J_{CP} = 16.145$)

and the notation used for these conformations is shown in Scheme 6).

The following two important points emerged:

(i) In the solid phase, the molecules invariably show 100% concertedness in the sense that for each conformer of the ester group, there is *only one* corresponding conformer of the triphenylphosphane fragment.

Table 4. ^{31}P NMR signals (^{1}H-decoupled) of complexes **3** in $CDCl_3$ (δ in ppm)

	a	**b**	**c**	**d**	**e**
3	57.30	57.22	57.43	57.56	57.78

Table 5. Experimental parameters relating to the X-ray diffraction measurements of complexes **3**

	a	**b**	**c**	**d**	**e** ($P\bar{1}$)	**e** ($P2_1/c$)
Empirical formula	$C_{24}H_{20}CoO_5P \cdot {}^{1}/_{2}\ C_4H_{10}O$	$C_{26}H_{24}CoO_5P$	$C_{26}H_{24}CoO_5P$	$C_{27}H_{26}CoO_5P$	$C_{29}H_{28}CoO_5P$	$C_{29}H_{28}CoO_5P$
Molecular mass	515.387	506.380	506.380	520.407	546.445	546.445
Temperature	r.t.	r.t.	125 K	r.t.	r.t.	125 K
Wavelength [Å]	0.71069	0.71069	0.71069	0.71069	0.71069	0.71069
Crystal system, space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
Unit cell dimensions:						
a [Å]	9.838(2)	9.575(1)	9.813(4)	13.789(3)	9.625(2)	9.968(4)
b [Å]	10.175(2)	18.169(2)	10.852(4)	11.406(3)	11.349(2)	21.094(8)
c [Å]	14.201(5)	14.662(2)	12.648(5)	17.854(4)	14.368(2)	13.215(6)
α [°]	73.71(2)	90	85.70(3)	90	102.30(1)	90
β [°]	70.40(2)	104.49(1)	77.75(3)	109.27(2)	108.24(1)	104.13(3)
γ [°]	87.65(2)	90	67.43(3)	90	103.38(1)	90
Volume [$Å^3$]	1283.0(6)	2469.5(5)	1212.0(8)	2651.0(1)	1379.2(4)	2694.6(1.6)
Z, calculated density [Mg/m^3]	2, 1.239	4, 1.362	2, 1.384	4, 1.304	2, 1.313	4, 1.345
Absorption coefficient [mm^{-1}]	0.76	0.79	0.81	0.74	0.72	0.73
Crystal size [mm^3]	0.27×0.25×0.18	0.48×0.33×0.27	0.30×0.26×0.18	0.48×0.36×0.27	0.32×0.27×0.21	0.23×0.19×0.17
θ range for data collection	$3° \leq 2\theta \leq 47°$	$3° \leq 2\theta \leq 55°$	$3° \leq 2\theta \leq 45°$	$3° \leq 2\theta \leq 50°$	$3° \leq 2\theta \leq 45°$	$3° \leq 2\theta \leq 48°$
Reflections collected/unique	4429/4223	6074/5655	4861/3170	4720/4305	5027/3572	4527/4205
Absorption correction	no	no	[a]	no	no	no
Refinement method	full matrix	full matrix	full matrix	full matrix	full matrix	full matrix
Final *R* indices [$I > 2\sigma(I)$]	0.0570	0.0486	0.0375	0.0435	0.0812	0.0438
R indices (all data; R_{ω})	0.1441	0.1340	0.0991	0.1153	0.2555	0.1150
Largest diff. peak and hole [$eÅ^{-3}$]	0.51 and −0.27	0.55 and −0.42	0.43 and −0.25	0.46 and −0.66	0.68 and −1.00	0.55 and −0.43
Instrument	Nicolet R3M/V	Nicolet R3M/V	Nicolet R3M/V	Siemens P4	Nicolet R3M/V	Nicolet R3M/V
Program	SHELXTL-PLUS; micro VAX II	SHELXTL-PLUS; micro VAX II	SHELXTL-PLUS; micro VAX II	SHELXTL-PLUS; SGI IRIS Indigo	SHELXTL-PLUS; micro VAX II	SHELXTL-PLUS; micro VAX II

[a] Empirical, ψ-scan in the 2θ range [°]: $3 \leq 2\theta \leq 50$; min./max. transmission: 0.72/0.87; $R_{merg.}$ before/after correction: 0.054/0.044.

(ii) The above mechanism excludes 50% of the statistically possible combinations, allowing only *re*,**M** and *si*,**P** for **3a**, **3c**, and **3d**, and only *re*,**P** and *si*,**M** for **3b** and for the two phases of **3e**.

This selection rule appears to be independent of (a) the number of molecules in the unit cell ($Z = 2$ or 4 for complexes **3**), and (b) the point group (as demonstrated by the behaviour of the two different phases of complexes **3e**). Recently, we performed an exhaustive molecular mechanical and quantum chemical analysis of the ethyl ester derivative[8a,16] EtOC(O)CH$_2$Co(CO)$_3$PPh$_3$. In this study, we found that the concerted conformational changes in this complex are controlled by a clockwork-analogous mechanism, where the displacements in the ester ligand are "felt" by the phosphane by transmission through the cogwheel-like Co(CO)$_3$ moiety.[16] This mechanism is responsible for the marked reduction in the number of statistically possible isomers to the number observed experimentally. The main goal of the present study has been to explore whether this concerted development of conformations is operative for other ester derivatives, with configurationally achiral groups in the ester fragment. The six structures reported in the present paper indicate a fairly general validity of this rule.

Beyond the correlations in the development of chiral conformations in molecules **3**, a strict correlation of these chiral conformations with the "secondary" centres of chirality, identified in the crystalline phases, has been observed. The (*R*) and (*S*) enantiomers (formed by H-bonding) of the ester alkyl α-C$_{sp}{}^3$ atoms (Scheme 4) in the Et and *n*Pr derivatives are 100% correlated to the corresponding *re*,**P** and *si*,**M** conformations, respectively.

These findings will hopefully aid detailed understanding of the mechanism of the intramolecular transfer of chiral information, which is of particular importance with regard to the design of third-generation (conformational) chiral catalysts and auxiliaries. We are extending our investigations to ester derivatives containing one or more configurational chiral centre(s) in the ester group or the phosphane ligand. The findings of these studies will be reported in subsequent papers.

Experimental Section

General Remarks: Starting materials were of commercial origin, with the exception of cyclohexyl bromoacetate[19] and octacarbonyldicobalt,[20] which were prepared by published procedures. − All

Table 6. Selected bond lengths and angles in complexes **3**

	Me *re***M**/*si***P**	*n*Pr *re***P**/*si***M**	*i*Pr *re***M**/*si***P**	*t*Bu *re***M**/*si***P**	*c*Hex1 *re***P**/*si***M**	*c*Hex2 *re***P**/*si***M**
Distances [Å]						
Co−P	2.213	2.216	2.208	2.214	2.211	2.217
Co−C$_{sp3}$	2.089	2.084	2.090	2.076	2.064	2.090
Co−C$_{sp}$ (*trans*)	1.767	1.777	1.788	1.791	1.703	1.793
Co−C$_{sp}$ (*gauche*-right)	1.778	1.778	1.789	1.790	1.781	1.788
Co−C$_{sp}$ (*gauche*-left)	1.788	1.787	1.800	1.773	1.775	1.789
C=O (ester)	1.206	1.197	1.212	1.190	1.218	1.213
C−O (ester)	1.332	1.331	1.352	1.350	1.344	1.356
C−O (*trans*)	1.138	1.137	1.145	1.132	1.187	1.143
C−O (*gauche*-right)	1.138	1.141	1.143	1.137	1.144	1.150
C−O (*gauche*-left)	1.132	1.133	1.212	1.142	1.150	1.143
Co−C$_{sp2}$	2.949	2.953	2.975	2.919	2.955	2.933
Angles [°]						
Co−C$_{sp3}$−C$_{sp2}$	110.8	111.6	111.9	108.9	112.8	109.4
P−Co−C$_{sp3}$	175.5	176.1	177.1	178.1	176.5	176.8
Co−P−C$_{ar}$ (I)	106.0	115.2	112.5	112.9	115.5	114.4
Co−P−C$_{ar}$ (II)	113.5	114.8	116.0	113.9	113.4	113.4
Co−P−C$_{ar}$ (III)	114.4	114.2	113.8	116.0	113.8	116.1
C$_{sp}$(*g*.-right)−Co−C$_{sp}$(*g*.-left)	117.3	119.9	117.8	126.7	120.7	125.1
C$_{sp}$(*trans*)−Co−C$_{sp}$(*g*. right)	120.7	119.2	120.4	114.2	120.7	119.5
C$_{sp}$(*g*.-left)−Co−C$_{sp}$(*trans*)	121.3	120.2	121.3	118.7	117.9	115.1
P−Co−C$_{sp}$ (*trans*)	92.0	92.5	92.3	95.0	92.3	94.6
P−Co−C$_{sp}$ (*gauche*-right)	92.5	93.2	91.4	90.9	92.2	89.8
P−Co−C$_{sp}$ (*gauche*-left)	93.2	92.5	93.7	91.5	93.3	92.0
C$_{sp}$ (*trans*)−Co−C$_{sp3}$	83.5	84.6	84.9	86.9	84.3	87.1
C$_{sp}$ (*gauche*-right)−Co−C$_{sp3}$	89.6	90.5	90.2	88.1	89.2	87.0
C$_{sp}$ (*gauche*-left)−Co−C$_{sp3}$	89.6	86.8	87.6	87.8	88.7	89.7
Dihedral angles [°]						
Co−C$_{sp3}$−C$_{sp2}$−O$_{sp3}$	−91/91	−76/76	−80/80	−91/91	−76/76	−93/93
Co−P−C$_{ar}$−C$_{ar}$(**I**)	43/−43	47/−47	55/−54	36/−36	−41/41	−38/38
Co−P−C$_{ar}$−C$_{ar}$(**II**)	41/−41	46/−46	43/−43	45/−45	−48/48	−52/52
Co−P−C$_{ar}$−C$_{ar}$(**III**)	46/−46	45/−45	41/−42	36/−36	−48/48	−38/38

operations were performed using standard Schlenk techniques.[21] − IR spectra were recorded with a Bruker FT-IR IFS 113V spectrometer. − ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with a Bruker AMX-400 instrument. − X-ray diffraction measurements were made with a Nicolet R3m/V four-circle diffractometer with Mo-K_α radiation at 298 K. Calculations were performed using the Bruker-AXS SHELXTL Vers. 5.10. Atomic scattering factors were taken from SHELXTL and ref.[22] Corrections for anomalous dispersion were made according to ref.[23] − For the preparation of the alkylcobalt complexes $[ROC(O)CH_2]Co(CO)_3PPh_3$, the procedures followed were essentially those described in ref.[8b] (Scheme 1).

Preparation of *c*HexOC(O)CH$_2$Co(CO)$_3$PPh$_3$ (3e): $Co_2(CO)_8$ (171 mg, 0.5 mmol) in Et_2O (15 mL) was reduced to $Na[Co(CO)_4]$ with Na/Hg. The resulting solution, containing 1 mmol of $Na[Co(CO)_4]$, was filtered into a Schlenk vessel under Ar and then cooled to −20 °C. Under stirring, cyclohexyl bromoacetate (221 mg, 1 mmol) was added in a single portion, which led to the immediate precipitation of white NaBr. Stirring was continued at this temperature for 4 h, in the course of which the colour of the solution gradually became more yellow and eventually turned brown. Thereafter, the solution was allowed to warm to room temperature and stirred for a further 1 h. A sample was taken (1 mL), which was analysed by IR spectroscopy in the 1600−2200 cm^{-1} range. This analysis showed the disappearance of the strong band due to $[Co(CO)_4]^-$ (at ca. 1900 cm^{-1}) and the emergence of a band system corresponding to an $RCo(CO)_4$-type complex,[9] further accompanied by an "organic" ν(C−O) absorption at ca. 1720−1710 cm^{-1}. This result indicated *c*HexOC(O)CH$_2$Co(CO)$_4$ (**1e**) to be the only carbonylcobalt species present in the reaction mixture. The solution was then filtered and to the filtrate, containing 1 mmol of complex **1e**, triphenylphosphane [$P(C_6H_5)_3$; 262 mg, 1 mmol] was added in a single portion at room temp. The resulting mixture was stirred for 3 h, in the course of which a gradual colour change from brown to light-yellow was observed. At this point, a sample (1 mL) was withdrawn and analysed by IR spectroscopy in the C−O stretching range (1600−2200 cm^{-1}); complete disappearance of the band system attributed to complex **1e** was observed, and two new band systems had emerged with an approximate intensity ratio of 1:9. The stronger band system, showing absorptions at higher wavenumbers, was attributed to the acylcobalt-type complex *c*HexOC(O)CH$_2$C(O)Co(CO)$_3$(PPh$_3$) (**2e**)[9] based on the fact that two acyl ν(C−O) bands were observed for this system. The weaker band pattern was assigned to *c*HexOC(O)CH$_2$Co(CO)$_3$(PPh$_3$) (**3e**) on the basis of comparisons with the spectra of previously characterized $ROC(O)CH_2Co(CO)_3PPh_3$ complexes.[6,8] The reaction mixture was subsequently warmed to 32 °C and stirred for a further 8 h at this temperature. After this treatment, a further sample was analysed by IR spectroscopy. This analysis showed the quantitative transformation of the acyl-type complex **2e** to the alkyl-type complex **3e**. The solvent was then evaporated at room temp. under reduced pressure. The crude product was recrystallized from Et$_2$O/*n*-hexane (ca. 6:1) to yield a yellow crystalline product (178 mg, 32.6%). This was characterized by elemental analyses, IR and NMR spectroscopy, and X-ray diffraction analysis. − $C_{29}H_{28}CoO_5P$ (546.445): calcd. C 63.74, H 5.16, Co 10.78, P 5.67; found C 63.9, H 5.4, Co 10.8, P 5.7. − X-ray diffraction analysis of this product revealed a $P\bar{1}$ phase (see later). The crude product obtained from an identical experiment was recrystallized from *n*-hexane. This operation yielded 168 mg (30.8%) of a yellow crystalline product, which was subsequently identified as belonging to the $P2_1/c$ phase. − Found C 63.8, H 5.3, Co 11.0, P 5.5.

Complexes 3a, 3b, 3c, and 3d: These were prepared by essentially the same procedure as described above. IR, ^{1}H, ^{13}C, and ^{31}P NMR spectroscopic data are listed in Tables 1, 2, 3, and 4. Experimental parameters relating to the X-ray diffraction measurements are shown in Table 5. Selected bond lengths and angles are collected in Table 6. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-163127 (**3a**) -163128 (**3b**), -163129 (**3c**), -163130 (**3d**), -163131 (**3e** monoclinic), -163132 (**3e** triclinic). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

3a: $C_{26}H_{22}CoO_{5.5}P$ [$\mathbf{3a}\cdot{}^1/_2(C_2H_5)_2O$] (515.387): calcd. C 60.95, H 4.33; found C 61.1, H 4.7.

3b: $C_{26}H_{24}CoO_5P$ (506.380): calcd. C 61.67, H 4.78; found C 62.1, H 5.0.

3c: $C_{26}H_{24}CoO_5P$ (506.380): calcd. C 61.67, H 4.78, Co 11.64, P 6.12; found C 61.9, H 5.1, Co 11.3, P 5.9.

3d: $C_{27}H_{26}O_5CoP$ (520.407): calcd. C 62.32, H 5.04, Co 11.32; found C 62.1, H 5.1, Co 10.8.

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