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Optically active transition metal compounds 113[1] Synthesis of chiral carbonylnitrosylcobalt complexes with four different unidentate ligands

Henri Brunner [a,*], Peter Faustmann [a], Bernhard Nuber [b]

[a] *Institut für Anorganische Chemie der Universität Regensburg, 93040, Regensburg, Germany*
[b] *Anorganisch-Chemisches Institut der Universität Heidelberg, 69120, Heidelberg, Germany*

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Abstract

In a two step synthesis pairs of diastereomers Co(CO)(NO)(L)(L*), which differ only in the configuration at the cobalt atom, are obtained from $Co(CO)_3(NO)$. L is a monodentate phosphite or phosphane and L* a monodentate optically active phosphane or isocyanide. For complex **8** (L = PPh_3, L = phenyl-tarpholane) a diastereomer ratio of 55:45 (**8a**:**8b**) is found after the synthesis. For all other complexes this ratio is 50:50. By crystallization it is possible to obtain samples enriched in one of the diastereomers of **1** (L = $P(OMe)_3$, L* = $PPh_2N(Me)CH(Me)(Ph)$), **2** (L = PPh_3, L* = CNCH(Me)(Ph)), **7** (L = PMe_2Ph, L* = glyphos) and **8**. The ratios achieved are 74:26 (**1a**:**1b**), 79:21 (**2a**:**2b**), 71:29 (**7a**:**7b**) and 74:26 (**8a**:**8b**). The crystal structures of six complexes were determined. For (S_{Co},S_C)-**2a**, (R_{Co},S_C)-**3b** and (S_{Co},R_C,R_C)-**8a** the absolute configuration could be established. The cobalt center is configurationally stable at room temperature. Epimerization is observed only at higher temperatures. **1a** epimerizes in toluene-d_8 at 82.2°C with a half life of $\tau_{1/2}$ = 43 h, **2a** in benzene-d_6 at 72.9°C with $\tau_{1/2}$ = 83 min and **7a** in benzene-d_6 at 70.0°C with $\tau_{1/2}$ = 77 min.

Keywords: Chirality; Cobalt(carbonyl)(nitrosyl) complexes; X-ray structure analysis; Absolute configuration; Epimerization

1. Introduction

Optically active organometallic complexes play an important role in the investigation of the stereochemical course of reactions [2,3]. We were interested in carbonylnitrosylcobalt complexes as they belong to the rare type of purely tetrahedral complexes. The racemates of $Co(CO)(NO)(PPh_3)(AsPh_3)$ and $K[Co(CO)(NO)(CN)(PPhR_2)]$ [4,5] as well as the mixture of diastereomers of $Co(CO)(NO)(PPh_3)(L^*)$, L* = optically active carbene [6,7], have been described in the literature. The only tetrahedral complexes, the isomers of which with respect to the different configuration at the metal center could be separated, are complexes of the type $Fe(CO)(NO)(NNAr)(PPh_2NRR^*)$ [8]. Most of the other optically active complexes containing a chiral metal center are half-sandwich complexes, i.e. they have octahedral geometry with η^5-H_5 or η^6-arene ligands occupying three facial coordination sites. In a preceding paper we have reported the synthesis of complexes of the type Co(CO)(NO)(LL*), LL* = optically active bisphosphane [1], and the separation of the corresponding diastereomers. Now we report the synthesis of new complexes of the type Co(CO)(NO)(L)(L*), in which L is a monodentate phosphite or phosphane and L* a monodentate optically active phosphane or isocyanide. The complexes are obtained as pairs of diastereomers which differ only in the configuration at the cobalt center. For some of the complexes it has been possible to enrich one diastereomer by repeated crystallization. By X-ray structure analysis the absolute configuration of three of the complexes could be determined.

* Corresponding author.
[1] For part 112 see ref. [1].

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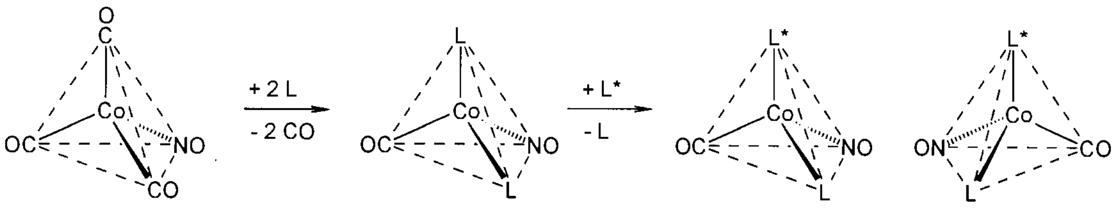


Scheme 1. Production of the diastereomers **a**/**b**.

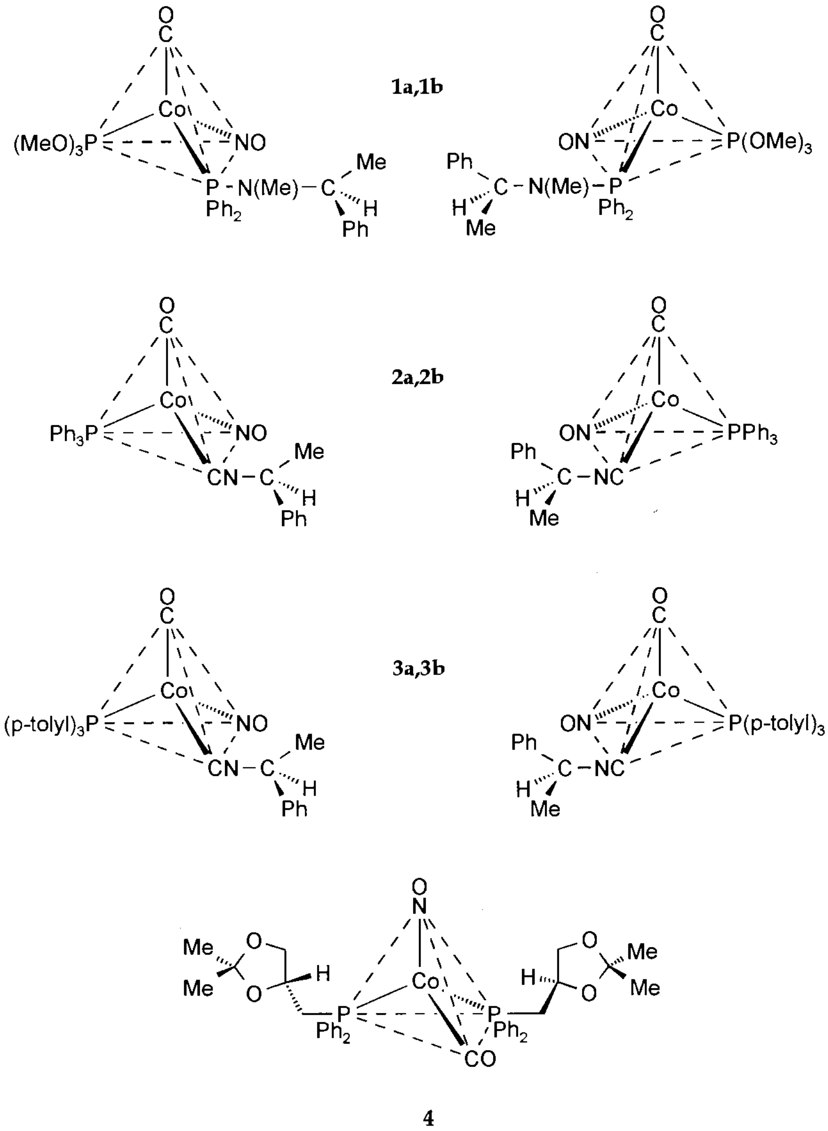
2. Results and discussion

Starting material for the synthesis of the new complexes is $Co(CO)_3(NO)$. The well known complexes of the type $Co(CO)(NO)L_2$, in which L is a phosphite or a phosphane, can be prepared easily and in high yields from $Co(CO)_3(NO)$ and an excess of the corresponding ligand [4]. Further reaction between $Co(CO)(NO)L_2$ and a small excess of a different ligand L* (L* = optically active phosphane or isocyanide) at a temperature above 60°C leads to mixtures of the diastereomers of Co(CO)(NO)(L)(L*) (Schemes 1–3). The best results were achieved in this substitution when the incoming ligand had better σ-donor properties compared to the leaving ligand. The sterical demands of the ligands, however, had less influence.

The products were purified by chromatography on silica. The analytical, IR and FD MS data for the new complexes **1**–**9** are summarized in Table 1.

The ratio of the diastereomers **a**/**b**, which differ only in the configuration at the cobalt atom, is determined by ^{1}H-NMR spectroscopy. In most cases the diastereomers were formed in a ratio of 50:50. Only for complex **8** the ratio differs from that value (**8a**:**8b** = 55:45). In accord with the results found for the diastereomeric complexes of the type Co(CO)(NO)(LL*), LL* = bidentate ligands, the diastereomers cannot be separated by chromatographic methods [1]. But with the complexes **1**, **2**, **7** and **8** we were able to obtain enriched samples by repeated crystallization. The ratios, which we achieved, were **1a**:**1b** = 74:26, **2a**:**2b** = 79:21, **7a**:**7b** = 71:29 and **8a**:**8b** = 74:26.

In complexes of the type Co(CO)(NO)(PP*), in which PP* is an optically active bisphosphane, epimerization with respect to the cobalt center occurred even at room temperature [1]. Under these conditions the new complexes proved to be configurationally stable. Only at temperatures above 50°C epimerization began. For the diastereomers **1a**, **1b**, **2a**, **2b** and **7a**, **7b** we measured the rate of the epimerization. For that purpose solutions of enriched samples of **1**, **2** and **7**, respectively, in benzene-d_6 or toluene-d_8 with concentrations of about 0.01 mol l^{-1} were prepared. These solutions were kept at defined temperatures in the range from 60°C up to 90°C. After given time intervals samples were taken. Before the ratio of diastereomers could be measured by ^{1}H-NMR it was necessary to filter the samples in order to remove small amounts of decomposition products. For all three complexes a diastereomer equilibrium of 50:50 was found. All reactions obeyed a first-order rate law. We found rate constants k of 6.06×10^{-6} s^{-1} ($\tau_{1/2} = 43$ h; **1a**, **1b** in toluene-d_8 at 82.2°C), 1.40×10^{-4} s^{-1} ($\tau_{1/2} = 83$ min; **2a**, **2b** in benzene-d_6 at 72.9°C) and 1.50×10^{-4} s^{-1} ($\tau_{1/2} = 77$ min; **7a**, **7b** in benzene-d_6 at 70.0°C). Measurements of the rate constants at different temperatures allowed the calculation of the activation enthalpie $\Delta H^{\neq}$ and entropie $\Delta S^{\neq}$. We found $\Delta H^{\neq} = 143$ kJ mol^{-1} and $\Delta S^{\neq} = 56$ J mol^{-1} K^{-1} (**1**), $\Delta H^{\neq} = 127$ kJ mol^{-1} and $\Delta S^{\neq} = 49$ J mol^{-1} K^{-1} (**2**) and $\Delta H^{\neq} = 123$ kJ mol^{-1} and $\Delta S^{\neq} = 38$ J mol^{-1} K^{-1} (**7**). In all cases we observed by-products during the reactions. For the reaction with the diastereomers **2a**, **2b** we were able to identify the by-products by NMR and FD mass spectroscopy. They proved to be the complexes $Co(CO)_2(NO)(PPh_3)$ and $Co(NO)(PPh_3)[CNCH(Me)(Ph)]_2$. The latter was also obtained as a by-product during the syntheses of **2** as it was described in a preceding paper [9]. The use of higher concentrations of **2** led to a small increase in the epimerization rate. On the other hand the addition of small amounts, even less than one equivalent, of triphenylphosphane or tri(p-tolyl)phosphane led to a substantial decrease of the reaction rate. Simultaneously, the number and the amount of by-products increased dramatically. On addition of 1.3 equivalents of tri(p-tolyl)phosphane we were able to identify 12 different cobalt complexes besides **2a**, **2b** by FD mass spectroscopy. Three complexes (**3a**, **3b**, $Co(NO)(PPh_3)[CNCH(Me)(Ph)]_2$ and $Co(NO)[P(p\text{-tolyl})_3][CNCH(Me)(Ph)]_2$) could also be detected by NMR. This huge number of by-products complicated the evaluation of the data obtained. Taking into account all the results it seems obvious that the epimerization of the Co(CO)(NO)(L)(L*) complexes follows a dissociative mechanism.



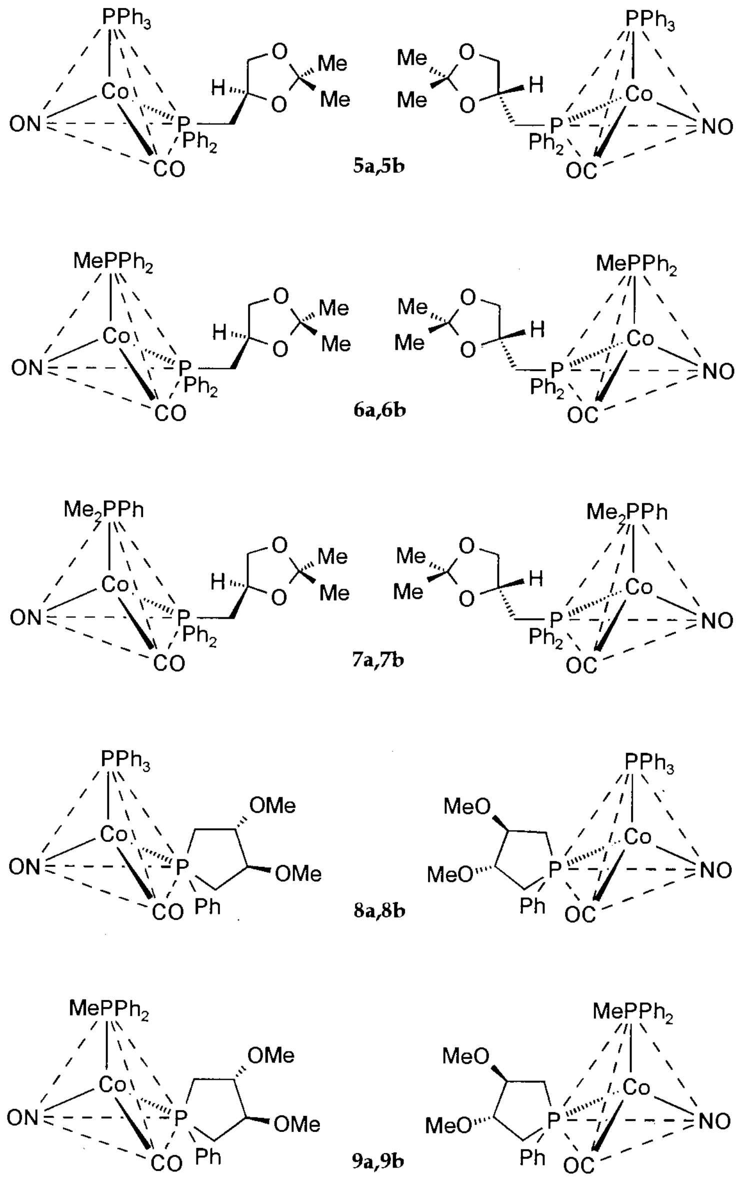
Scheme 2. The diastereomers **1a**,**1b**, **2a**,**2b**, **3a**,**3b** and complex **4**.

3. X-ray structure analyses

X-ray structure analyses were performed with the complexes **1**, **2a**, **3b**, **4**, **7** and **8a**. Table 2 gives details of the data collection, structure refinement and crystal data of the six complexes.

In all cases the expected distorted tetrahedral coordination geometry about the cobalt center was found. For the complexes **1**, **4** and **7** the CO and NO groups could not be differentiated. For the complexes **2a**, **3b** and **8a**, however, this was possible. Thus, the absolute configuration of these complexes could be determined. This was done by refinement of the least-squares variable η (complexes **2a**, $\eta = 1.3(4)$ and **8a**, $\eta = 1.1(1)$) and the Flack parameter (complex **3b**, $x = 0.01(2)$), respectively. The measured crystal of **2a** is assigned the configuration (S_{Co},S_C), **3b** is assigned (R_{Co},S_C) and **8a** is assigned (S_{Co},R_C,R_C). By a comparison of the CD spectra of the measured crystal **2a** and the enriched sample **2a**:**2b** = 79:21, from which it was taken, we could confirm that the measured crystal is from the enriched diastereomer. Due to the small crystal sizes, this test was not possible with **3b** and **8a**. Figs. 1–6 show the structures of all six complexes. In Tables 3 and 4 selected bond distances and angles are listed.

All bond distances are in the normal range found for other Co(CO)(NO) complexes [7,10,11]. For the Co–C(CO) distances we found values from 1.633 to 1.725 Å and for the Co–N(NO) distances values from 1.629 to 1.725 Å. The C–O distances lie between 1.126 and 1.189 Å and the N–O distances between 1.147 and 1.205 Å, respectively. As expected the CO and NO groups are found to be nearly linear. The angles range from 171.8 to 178.5°. In accord with known complexes the angles (OC)C–Co–N(NO) are the largest around the Co center, they vary from 118.3 to 124.3°. The two



Scheme 3. The diastereomers **5a,5b**–**9a,9b**.

complexes containing the isocyanide ligand deviate markedly from each other. Whereas **3b** shows normal values for all distances and angles, for **2a** a long Co–C(CN) bond (2.003 Å compared to 1.860 Å in **3b**) and a short C–N bond (1.143 Å compared to 1.155 Å) was found. On the other hand the Co–C(CO) and the Co–N(NO) bonds in **2a** are shorter than in **3b** and the C–O and N–O bonds are longer. These results indicate that in **2a** the CO and NO groups act as stronger π-acceptors than in **3b**, though the two complexes differ only in the phosphane ligand (triphenylphosphane in **2a** and tri(p-tolyl)phosphane in **3b**). Furthermore, in the unit cell of **3b** there are two independent molecules. Surprisingly, these molecules are diastereomeric to each other as they show opposite sense in the chirality of the tritolylphosphane propeller (Fig. 3).

4. Experimental section

All the complexes were prepared under an atmosphere of dried nitrogen. Solvents were dried and distilled prior to use, according to standard procedures. Infrared spectra were recorded on a Perkin–Elmer Paragon 1000 PC FT–IR and a Beckman IR 4240 spectrometer. ^{1}H- and ^{31}P-NMR spectra were obtained on a Bruker AC 250 and a Bruker ARX 400 spectrometer [250 or 400 MHz (^{1}H) and 162 MHz (^{31}P)]. Chemical shifts are in ppm downfield from TMS or 85% H_3PO_4, respectively. FD mass spectra were determined on a Finnigan MAT 95 instrument. Optical rotations were measured with a Perkin–Elmer 241 polarimeter. Microanalyses were carried out by the microanalytical laboratory of the University of Regensburg.

Table 1
IR spectroscopic, analytical and FD MS data for the (carbonyl)(nitrosyl) cobalt complexes **1**–**9**

Co(CO)(NO)(L)(L*) L, L* =	IR [cm^{-1}][a] ν(CO)	ν(NO)	Analyses [%][b] C	H	N	FD MS[c] [e/m] M^{+d}	formula
1 $P(OMe)_3$, $PPh_2N(Me)C^*$[e]	1960	1725	53.69 (53.58)	5.55 (5.58)	5.22 (5.00)	560.2 (560.41)	$C_{25}H_{31}CoN_2O_5P_2$
2 PPh_3, CNC*[e,f]	1959, 1941	1715, 1703	65.90 (65.89)	4.74 (4.74)	5.76 (5.49)	510.2 (510.41)	$C_{28}H_{24}CoN_2O_2P$
3 P(*p*-tolyl)$_3$, CNC*[e,g]	1966, 1944	1715, 1705	67.46 (67.39)	5.49 (5.47)	5.03 (5.07)	552.1 (552.49)	$C_{31}H_{30}CoN_2O_2P$
4 glyphos	1945	1710	61.89 (61.93)	6.00 (5.90)	2.01 (1.95)	717.1 (717.63)	$C_{37}H_{42}CoNO_6P_2$
5 PPh_3, glyphos	1920	1690	65.29 (65.39)	5.26 (5.34)	2.07 (2.06)	679.4 (679.58)	$C_{37}H_{36}CoNO_4P_2$
6 PPh_2Me, glyphos	1930	1680	61.99 (62.24)	5.45 (5.55)	2.31 (2.27)	617.1 (617.51)	$C_{32}H_{34}CoNO_4P_2$
7 PMe_2Ph, glyphos	1920	1660	58.31 (58.39)	5.85 (5.81)	2.50 (2.52)	555.2 (555.44)	$C_{27}H_{32}CoNO_4P_2$
8 PPh_3, phenyl-tarpholane	1941, 1925	1703, 1690	61.52 (61.70)	5.40 (5.34)	2.36 (2.32)	603.2 (603.48)	$C_{31}H_{32}CoNO_4P_2$
9 PPh_2Me, phenyl-tarpholane	1937, 1925	1697, 1683	57.64 (57.68)	5.75 (5.59)	2.52 (2.59)	541.1 (541.41)	$C_{26}H_{30}CoNO_4P_2$

[a] KBr pellets, strong absorptions.
[b] Calculated values in parentheses.
[c] Solvent toluene.
[d] Calculated M in parentheses.
[e] C* = (*S*)-CH(Me)(Ph).
[f] ν(CN) 2129 cm^{-1}.
[g] ν(CN) 2127 cm^{-1}.

$Co(CO)_3(NO)$ was prepared by the method of Hieber [12]. It was stored under nitrogen at −25°C and not further purified prior to use. The complexes $Co(CO)(NO)[P(OMe)_3]_2$, $Co(CO)(NO)(PPh_3)_2$, Co(CO)(NO)[P(*p*-tolyl)$_3$]$_2$, $Co(CO)(NO)(PPh_2Me)_2$ and $Co(CO)(NO)(PMe_2Ph)_2$ were prepared according to literature methods [4,11,13]. The preparation of the four ligands was done by the methods indicated in the individual procedures.

4.1. *$Co(CO)(NO)[P(OMe)_3][PPh_2N(Me)CH(Me)(Ph)]$ **1a**, **1b***

A solution of $Co(CO)(NO)[P(OMe)_3]_2$ (5.00 g, 13.7 mmol) and (*S*)-(+)-*N*-Methyl-*N*-1-phenylethylamino-diphenylphosphane [14] (8.05 g, 25.2 mmol) in 40 ml of toluene was stirred for 48 h at 100°C. After removal of the solvent the residue was chromatographed on silica. Elution with toluene/petroleum ether 40–60 2:1 afforded three red or reddish brown bands. From the first band the by-product Co(CO)(NO)[PPh_2N(Me)CH-(Me)(Ph)]$_2$ (5%) and from the third band the remaining $Co(CO)(NO)[P(OMe)_3]_2$ (23%) were obtained. The second band provided the product **1a**, **1b** as a red powder after evaporating the solvent. Yield: 2.61 g (34%), molar ratio **1a**:**1b** = 50:50, m.p. 71–72°C. $[\alpha]_D^{24} = -8$ (c 0.878, CH_2Cl_2). ^{1}H-NMR ($CDCl_3$): δ (ppm, *J* (Hz)) 1.44 (d, $^3J_{HH}$ 6.9, 3H, CH_3), 2.14 (d, $^3J_{PH}$ 6.4, 1.5H, NCH_3 (**1a**)), 2.15 (d, $^3J_{PH}$ 6.4, 1.5H, NCH_3 (**1b**)), 3.24 (d, $^3J_{PH}$ 12.0, 4.5H, OCH_3 (**1a**)), 3.27 (d, $^3J_{PH}$ 12.0, 4.5H, OCH_3 (**1b**)), 5.69 (m, 1H, CH), 7.21–7.76 (m, 15H, phenyl-H). ^{31}P-NMR ($CDCl_3$): δ (ppm) 118 (br, 1P, P–N), 188 (br, 1P, P–O).

4.1.1. *Separation of the diastereomers*

At −18°C pentane was condensed into a solution of 470 mg of **1a**:**1b** = 50:50 in 6 ml of ether. After one week red crystals were obtained containing **1a**:**1b** in a molar ratio of 74:26. Yield: 179 mg (38%), m.p. 82°C. $[\alpha]_D^{24} = +44$ (c 0.856, CH_2Cl_2). From the mother liquor a red solid can be isolated containing the isomers **1a**:**1b** in a molar ratio of 35:65. Yield: 240 mg (51%), m.p. 68–69°C. $[\alpha]_D^{24} = -45$ (c 1.077, CH_2Cl_2).

4.2. *$Co(CO)(NO)(PPh_3)[CNCH(Me)(Ph)]$ **2a**,**2b***

A mixture of $Co(CO)(NO)(PPh_3)_2$ (2.00 g, 3.12 mmol) and (*S*)-(−)-CNCH(Me)(Ph) [15] (0.43 g, 3.28 mmol) in 40 ml of toluene was stirred for 4 h at 90°C. The solvent was evaporated and the residue chromatographed on silica. With toluene/petroleum ether 40–60 2:1 a red band was eluted which provided the

Table 2
Summary of crystal data, data collection and structure refinement for **1**, **2a**, **3b**, **4**, **7** and **8a**

Crystal parameters						
Complex (formula)	**1** ($C_{25}H_{31}CoN_2O_5P_2$)	**2a** ($C_{28}H_{24}CoN_2O_2P$)	**3b** ($C_{31}H_{30}CoN_2O_2P$)	**4** ($C_{37}H_{42}CoNO_6P_2$)	**7** ($C_{27}H_{32}CoNO_4P_2$)	**8a** ($C_{31}H_{32}CoNO_4P_2$)
Color and shape	Red, irregular	Red, irregular	Red–brown, plates	Red, bipyramidal	Red, octahedral	Red, prismatic
Size [mm]	0.23 × 0.31 × 0.38	0.27 × 0.32 × 0.46	0.25 × 0.40 × 0.75	0.30 × 0.30 × 0.65	0.45 × 0.75 × 0.99	0.25 × 0.30 × 0.55
Crystal system	Rhombic	Hexagonal	Triclinic*	Tetragonal	Rhombic	Hexagonal
Space group	P2.12.12.1 (19)	P3.1 (144)	P1 (1)	P4.12.12 (92)	P2.12.12.1 (19)	P3.1 (144)
a [Å]	9.421(5)	9.914(1)	10.265(5)	10.357(5)	10.000(5)	9.486(3)
b [Å]	12.047(6)	9.914(1)	10.543(5)	10.357(5)	10.485(5)	9.486(3)
c [Å]	24.37(1)	22.790(5)	15.889(8)	33.99(2)	26.38(1)	29.02(1)
Z; $D_{calc.}$ [g cm^{-3}]; V [Å^3]	4; 1.35; 2766	3; 1.31; 1940	2 × 1; 1.26; 1452	4; 1.31; 3646	4; 1.33; 2766	3; 1.33; 2260
F(000)	1168	792	576	1504	1160	942
μ [mm^{-1}]	0.77	0.75	0.67	0.60	0.77	0.71
Data collection						
hkl ranges	0–11; 0–14; 0–28	0–10; −10–0; 0–24	−14–14; −14–14; 0–22	0–14; 0–10; 0–46	0–14; 0–14; 0–37	0–12; −12–0; 0–35
2θ range [°]	3.0–47.5	3.0–45.0	3.0–60.0	3.0–57.5	3.0–60.0	3.0–50.0
No. of unique reflections	4172	1949	8477	3546	5579	2717
No. of observed reflections with $I>2.5\sigma(I)$	1924	800	5942 ($I>2\sigma_I$)	1864	4887	1908
Min. transmission factor[a]	0.82	0.82	0.90	0.85	0.81	0.95
Data refinement						
No. of reflections and 2θ range [°] for absorption correction	5; 5.0–16.0	5; 7.0–23.0	8; 8.9–42.0	5; 5.0–24.0	8; 8.0–46.0	7; 8.0–39.0
No. of LS-parameters	191	139	687	214	317	352
Largest shift/e.s.d. in final cycle	0.003	0.004	0.006	0.001	0.01	0.005
$\Delta\rho_{min}$; $\Delta\rho_{max}$ [e Å^{-3}]	−0.50; 0.69	−0.33; 0.32	−0.30; 0.39	−0.43; 0.44	−0. 56; 0.42	−0.37; 0.49
R-merge; R[b]; Rw[c]	0.020; 0.059; 0.046	0.024; 0.072; 0.059	—; 0.053; 0.039	0.025; 0.047; 0.032	—; 0.037; 0.029	0.042; 0.056; 0.043

* $\alpha = 75.99(2)°$; $\beta = 78.76(2)°$; $\gamma = 60.95(2)°$.
[a] Max. transmission factor 1.00 for all complexes.
[b] $R = \Sigma \| F_o - F_c \| / |F_c|$.
[c] $Rw = \Sigma \| F_o| - |F_c\| w^{1/2} / |F_c| w^{1/2}$, $w = 1/\sigma^2(F_o)$.

diastereomers **2a**, **2b**. Further elution with a larger amount of toluene afforded the by-products $Co(NO)(PPh_3)_2$[CNCH(Me)(Ph)] and $Co(NO)(PPh_3)$-$[CNCH(Me)(Ph)]_2$, which have been described in a preceding paper [9]. Yield: 1.04 g (65%), molar ratio **2a**:**2b** = 50:50, m.p. 103–104°C. $[\alpha]_D^{23} = +72$ (c 0.616, CH_2Cl_2). ^{1}H-NMR (C_6D_6): δ (ppm, J (Hz)) 0.88 (d, $^3J_{HH}$ 6.8, 1.5H, CH_3 (**2b**)); 0.91 (d, $^3J_{HH}$ 6.8, 1.5H, CH_3 (**2a**)); 3.98–4.04 (2 dq, $^5J_{PH}$ 2.2, $^3J_{HH}$ 6.8, 1H, CH); 6.69–6.75 (m, 2H, phenyl-H_{ortho}); 6.89–7.03 (m, 12H, phenyl-H); 7.61–7.69 (m, 6H, P-phenyl-H_{ortho}). ^{31}P-NMR (C_6D_6): δ (ppm) 60 (br).

4.2.1. Separation of the diastereomers

At −25°C a small amount of pentane was condensed into a solution of 1 g of **2a**:**2b** = 50:50 in 6 ml of toluene. After several days dark red crystals formed with which this procedure was repeated once. Finally crystals were obtained containing the diastereomers **2a**:**2b** in a molar ratio of 79:21. Crystals from this sample were suitable for X-ray analysis. Yield: 179 mg (18%), m.p. 112°C. $[\alpha]_D^{22} = +115$ (c 0.899, CH_2Cl_2).

4.3. Co(CO)(NO)[P(p-tolyl)$_3$][CNCH(Me)(Ph)] **3a**,**3b**

Co(CO)(NO)[P(p-tolyl)$_3$]$_2$ (1.10 g, 1.52 mmol) and (S)-(−)-CNCH(Me)(Ph) (0.23 g, 1.78 mmol) were treated the same way as described above for **2a**, **2b**. After recrystallization the complex **3a**, **3b** was obtained as dark red crystals. Yield: 428 mg (51%), molar ratio **3a**:**3b** = 50:50, m.p. 120°C. ^{1}H-NMR (C_6D_6): δ (ppm, J (Hz)) 0.95, 0.98 (2 d, $^3J_{HH}$ 6.8, 3H, CH_3); 1.98 (s, 9H, aryl-CH_3); 4.05–4.13 (m, 1H, CH); 6.73–6.78 (m, 2H, phenyl-H^{ortho}); 6.89–6.98 (m, 9H, phenyl-H); 7.66–7.70

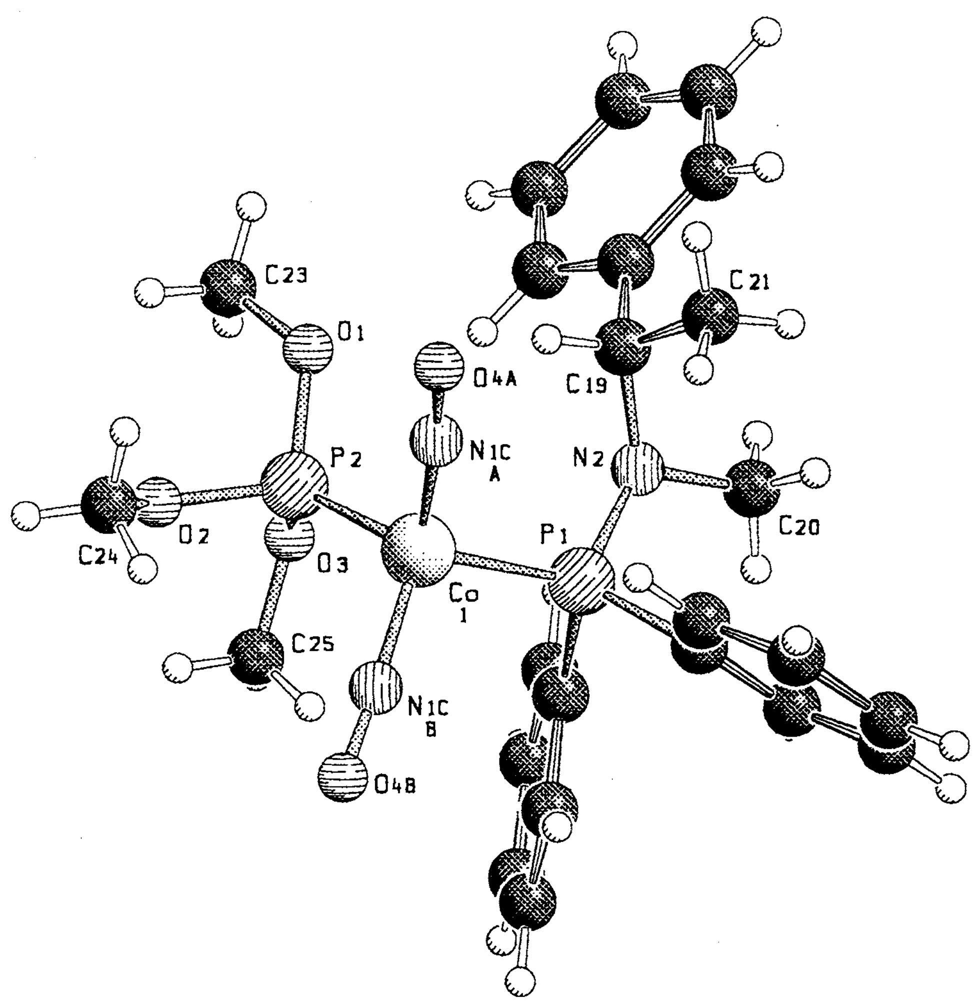


Fig. 1. SCHAKAL view of the molecular structure of Co(CO)(NO)[P(OMe)$_3$][(*S*)-PPh$_2$N(Me)CH(Me)(Ph)] **1**. Only selected labels are shown for clarity [19].

(m, 6H, P-aryl-H^{ortho}). ^{31}P-NMR (C_6D_6): δ (ppm) 57 (br).

4.4. *Co(CO)(NO)(glyphos)$_2$ **4***

At 0°C Co(CO)$_3$(NO) (0.88 g, 5.10 mmol) was added to a solution of (*R*)-(+)-glyphos [16] (3.44 g, 11.5 mmol) in 20 ml of toluene. The resulting orange solution was slowly warmed up to 85°C and kept at this temperature for 21 h. During the reaction the colour changed to dark red. The complex **4** was obtained as a reddish brown powder after adding pentane to the solution and cooling it to 0°C. Recrystallization from thf/ether/pentane 1:5:30 afforded red crystals. Yield: 2.69 g (74%), m.p. 104–106°C. $[\alpha]_D^{22} = +12$ (c 1.00, CH_2Cl_2). ^{1}H-NMR ($CDCl_3$): δ (ppm, *J* (Hz)) 1.17–1.19 (4 s, 12H, CH$_3$); 2.01 (ddd, $^2J_{HH}$ 13.5, $^2J_{PH}$ 8.7, $^3J_{HH}$ 8.5, 1H, PCH$_2$); 2.14 (A-part of an ABMX-system, 1H, PCH$'_2$); 2.22–2.33 (m, 2H, PCH$_2$ and PCH$'_2$)*; 2.77 (dd, $^2J_{HH}$ 8.1, $^3J_{HH}$ 7.6, 1H, OCH$_2$); 2.83 (dd, $^2J_{HH}$ 8.1, $^3J_{HH}$ 7.7, 1H, OCH$'_2$); 3.37 (dd, $^2J_{HH}$ 8.1, $^3J_{HH}$ 5.7, 1H, OCH$_2$); 3.45 (dd, $^2J_{HH}$ 8.1, $^3J_{HH}$ 5.6, 1H, OCH$'_2$); 3.93–4.06 (m, 2H, CH and CH′); 7.20–7.45 (m, 20H, phenyl-H)*. ^{1}H{^{31}P}-NMR: 2.26 (B-part of an ABX-system, 1H, PCH$'_2$); 2.31 (dd, $^2J_{HH}$ 13.5, $^3J_{HH}$ 4.5, 1H, PCH$_2$). ^{31}P-NMR ($CDCl_3$): δ (ppm) 42 (br).

4.5. *Co(CO)(NO)(PPh$_3$)(glyphos) **5a**, **5b***

A mixture of Co(CO)(NO)(PPh$_3$)$_2$ (1.19 g, 1.85 mmol) and (*R*)-(+)-glyphos (0.59 g, 1.96 mmol) in 30 ml of toluene was stirred for 4 h at 75°C. After evaporation of the solvent the residue was chromatographed on silica. Elution with ether/petroleum ether 40–60 2:7 afforded three red bands. The first band contained the remaining Co(CO)(NO)(PPh$_3$)$_2$ and the third band the complex **4** as a by-product. After removal of the solvent the diastereomers **5a**, **5b** were obtained as a reddish brown solid from the second band. Yield: 620 mg (49%), molar ratio **5a**:**5b** = 50:50, m.p. 122–123°C. $[\alpha]_D^{22} = -72$ (c 0.95, CH_2Cl_2). ^{1}H-NMR ($CDCl_3$): δ (ppm, *J* (Hz)) 1.19 (s, 1.5H, CH$_3$ (**5a**)); 1.21 (s, 1.5H,

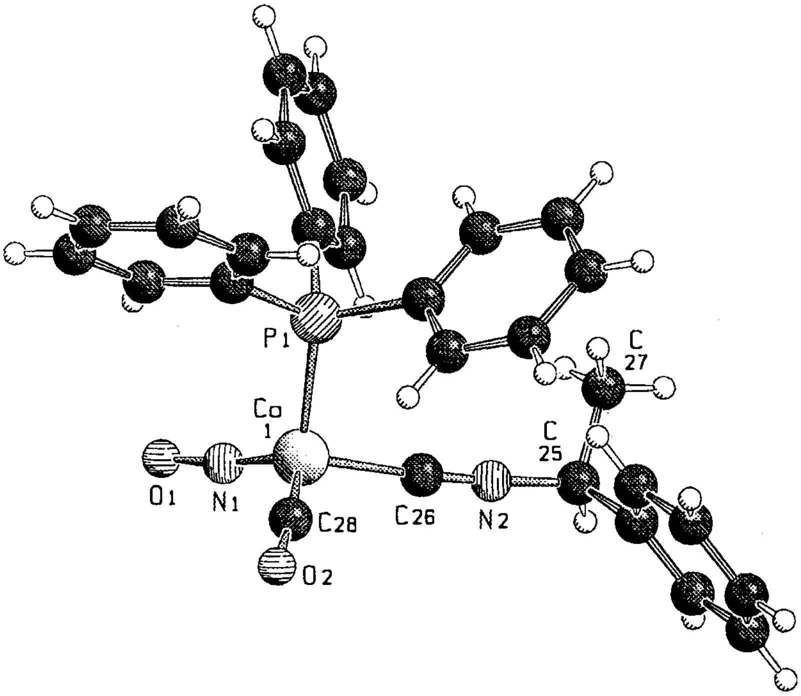


Fig. 2. SCHAKAL view of the molecular structure of (S_{Co},S_C)-Co(CO)(NO)(PPh_3)[CNCH(Me)(Ph)] **2a**. Only selected labels are shown for clarity.

CH_3 (**5b**)); 1.23 (s, 1.5H, CH_3 (**5a**)); 1.24 (s, 1.5H, CH_3 (**5b**)); 2.08–2.19 (A-parts of 2 ABX-systems, 1H, PCH_2); 2.24–2.31 (B-part of an ABX-system, 0.5H; PCH_2 (**5a**)); 2.41–2.47 (B-part of an ABX-system, 0.5H, PCH_2 (**5b**)); 2.79 (dd, $^2J_{HH}$ 8.2, $^3J_{HH}$ 7.9, 0.5H, OCH_2 (**5b**)); 2.84 (dd, $^2J_{HH}$ 8.2, $^3J_{HH}$ 7.9, 0.5H, OCH_2 (**5a**)); 3.35 (dd, $^2J_{HH}$ 8.2, $^3J_{HH}$ 5.7, 0.5H, OCH_2 (**5b**)); 3.41 (dd, $^2J_{HH}$ 8.2, $^3J_{HH}$ 5.7, 0.5H, OCH_2 (**5a**)); 4.02–4.10 (m, 0.5H, CH (**5a**)); 4.15–4.23 (m, 0.5H, CH (**5b**)); 7.14–7.48 (m, 25H, phenyl-H). ^{31}P-NMR ($CDCl_3$): δ (ppm) 43 (br, glyphos-P); 57 (br, PPh_3).

4.6. *Co(CO)(NO)(PPh_2Me)(glyphos)* ***6a***, ***6b***

A solution of Co(CO)(NO)(glyphos)$_2$ **4** (960 mg, 1.34 mmol) and PPh_2Me (430 mg, 2.15 mmol) in 20 ml of toluene was stirred for 5 h at 90°C. After removal of the solvent the residue was chromatographed on silica. Elution with CH_2Cl_2 afforded three red bands. From the first band the by-product Co(CO)NO)(PPh_2Me)$_2$ and from the third band the remaining **4** were isolated. The diastereomers **6a**, **6b** were obtained as a reddish brown solid from the second band after evaporating the solvent. Yield: 372 mg (45%), molar ratio **6a**:**6b** = 50:50, m.p. 95–96°C. $[\alpha]_D^{22} = -50$ (c 0.951, CH_2Cl_2). ^{1}H-NMR ($CDCl_3$): δ (ppm, J (Hz)) 1.20–1.26 (m, 9H, CH_3); 2.09–2.24 (m, 1H, PCH_2)*; 2.38–2.46 (m, 1H, PCH_2)*; 2.87 (dd, $^2J_{HH}$ 8.3, $^3J_{HH}$ 7.3, 0.5H, OCH_2); 2.97 (dd, $^2J_{HH}$ 8.3, $^3J_{HH}$ 7.3, 0.5H, OCH_2); 3.47 (dd, $^2J_{HH}$ 8.3, $^3J_{HH}$ 5.7, 0.5H, OCH_2); 3.53 (dd, $^2J_{HH}$ 8.3, $^3J_{HH}$ 5.7, 0.5H, OCH_2); 4.06–4.14 (m, 0.5H, CH); 4.15–4.22 (m, 0.5H, CH); 7.18–7.52 (m, 20H, phenyl-H)*. ^{1}H{^{31}P}-NMR: 2.13 (dd, $^2J_{HH}$ 13.3, $^3J_{HH}$ 8.6, 0.5H, PCH_2); 2.20 (dd, $^2J_{HH}$ 13.3, $^3J_{HH}$ 9.2, 0.5H, PCH_2); 2.42, 2.43 (2 dd, $^2J_{HH}$ 13.3, $^3J_{HH}$ 4.3, 1H, PCH_2). ^{31}P-NMR ($CDCl_3$): δ (ppm) 38 (br, PPh_2Me); 44 (br, glyphos-P).

4.7. *Co(CO)(NO)(PMe_2Ph)(glyphos)* ***7a***, ***7b***

In a mixture of 15 ml of thf and 15 ml of toluene Co(CO)(NO)(glyphos)$_2$ **4** (1.32 g, 1.84 mmol) and PMe_2Ph (2.18 g, 15.8 mmol) were dissolved. This solution was refluxed for 4 h. After evaporating the solvent the resulting oil was chromatographed on silica with ether/petroleum ether 40–60 1:5. During the chromatography the amount of ether was slowly raised up to 2:1. Three red bands separated. The first one afforded the by-product Co(CO)(NO)(PMe_2Ph)$_2$ and the third one the remaining **4**. After removal of the solvent the diastereomers **7a**, **7b** were obtained as a red solid. Yield: 470 mg (46%), molar ratio **7a**:**7b** = 50:50, m.p. 75–77°C. $[\alpha]_D^{22} = -34$ (c 0.900, CH_2Cl_2). ^{1}H-NMR (C_6D_6): δ (ppm, J (Hz)) 0.98, 0.99 (2 d, $^2J_{PH}$ 7.4, 3H, PCH_3); 1.17 (d, $^2J_{PH}$ 7.5, 3H, PCH_3); 1.24 (s, 1.5H, CH_3 (**7b**)); 1.28 (s, 1.5H, CH_3 (**7a**)); 1.31 (s, 1.5H, CH_3 (**7b**)); 1.34 (s, 1.5H, CH_3 (**7a**)); 2.18–2.31 (m, 1H, PCH_2); 2.60 (ddd, $^2J_{HH}$ 13.6, $^2J_{PH}$ 9.2, $^3J_{HH}$ 4.9, 0.5H, PCH_2 (**7b**)); 2.67 (ddd, $^2J_{HH}$ 13.5, $^2J_{PH}$ 8.6, $^3J_{HH}$ 4.5, 0.5H, PCH_2 (**7a**)); 3.09 (dd, $^2J_{HH}$ 8.1, $^3J_{HH}$ 7.4, 0.5H, OCH_2 (**7a**)); 3.18 (dd, $^2J_{HH}$ 8.2, $^3J_{HH}$ 7.2, 0.5H, OCH_2 (**7b**)); 3.66–3.72 (m, 1H, OCH_2); 4.46–4.51 (m, 0.5H, CH (**7b**));

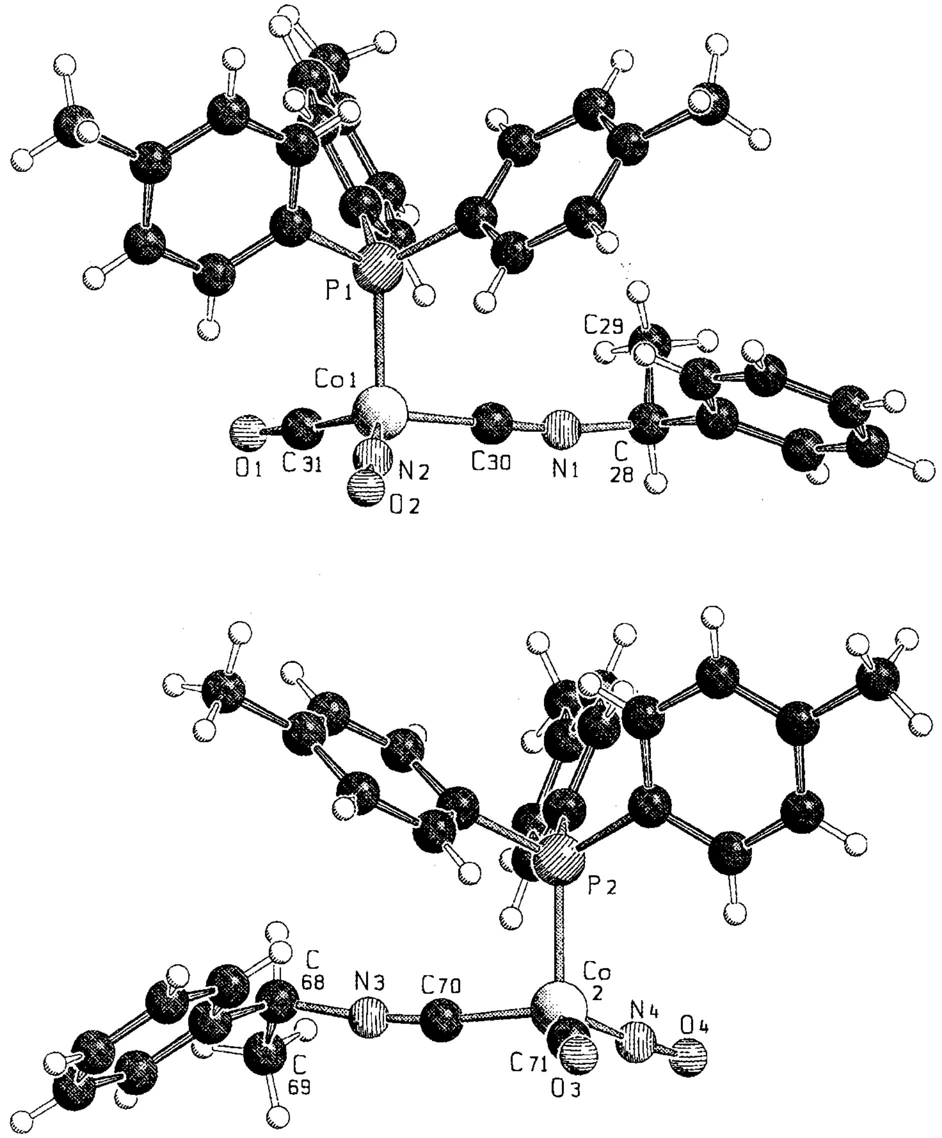


Fig. 3. SCHAKAL view of the molecular structures of the two independent molecules in the unit cell of (R_{Co},S_C)-Co(CO)(NO)[P(*p*-tolyl)$_3$][CNCH(Me)(Ph)] **3b** (above: P chirality of the propeller, bottom: *M* chirality). Only selected labels are shown for clarity.

4.57–4.65 (m, 0.5H, CH (**7a**)); 6.88–7.08 (m, 9H, phenyl-H); 7.25–7.58 (m, 6H, phenyl-H). ^{31}P-NMR (C_6D_6): δ (ppm) 19 (br, PMe_2Ph); 46 (br, glyphos-P).

4.7.1. Separation of the diastereomers

A solution of 200 mg of **7a**:**7b** = 50:50 in 10 ml of ether and 3 ml of pentane was cooled to −25°C. After one week red crystals formed with which this procedure was repeated once. Finally, crystals were obtained containing the diastereomers **7a**:**7b** in a molar ratio of 71:29. Crystals from this sample were suitable for X-ray analysis. Yield: 96 mg (48%), m.p. 90–91°C. $[\alpha]_D^{22} = -1$ (c 0.905, CH_2Cl_2).

4.8. Co(CO)(NO)(PPh_3)(phenyl-tarpholane) *8a*,*8b*

A solution of Co(CO)(NO)$(PPh_3)_2$ (1.30 g, 2.03 mmol) and (*R*,*R*)-(+)-phenyl-tarpholane [17] (0.44 g, 1.96 mmol) in 25 ml of toluene was refluxed for 9 h. The solvent was evaporated and the residue was chromatographed on silica. With toluene/petroleum ether 40–60 1:1 remaining Co(CO)(NO)$(PPh_3)_2$ was eluted. Further elution with toluene/thf 1:1 afforded a second red band which provided the diastereomers **8a**, **8b** as a red powder after removal of the solvent. Yield: 355 mg (30%), molar ratio **8a**:**8b** = 55:45, m.p. 145–146°C. $[\alpha]_D^{22} = +31$ (c 0.837, CH_2Cl_2). ^{1}H-NMR ($CDCl_3$): δ

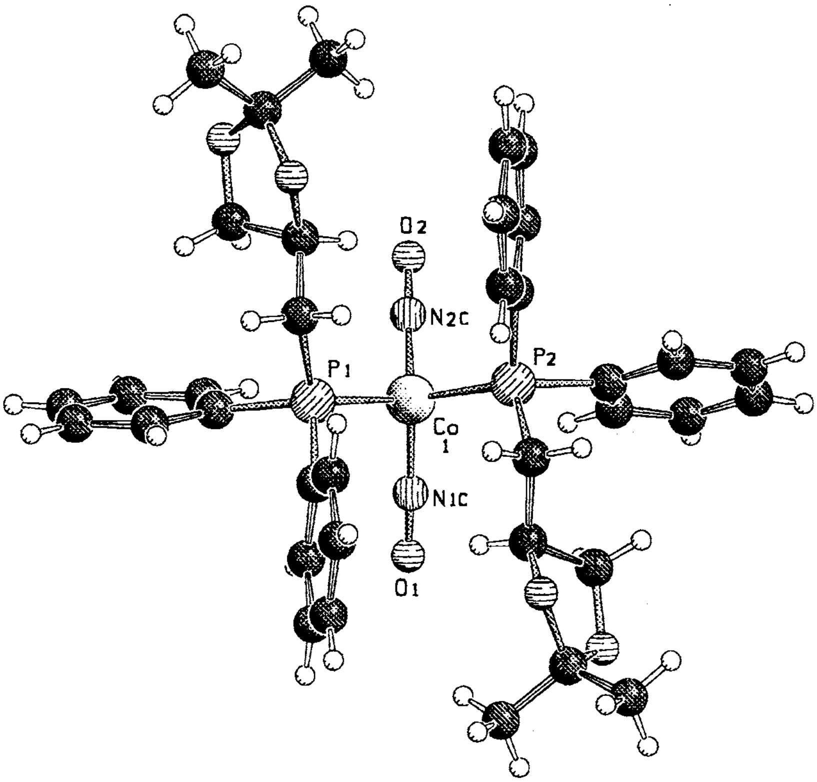


Fig. 4. SCHAKAL view of the molecular structure of Co(CO)(NO)[(*R*)-glyphos]$_2$ **4**. Only selected labels are shown for clarity.

(ppm, J (Hz)) 1.59 (ddd, $^2J_{HH}$ 14.5, $^3J_{HH}$ 8.1, $^2J_{PH}$ 2.5, 0.45H, CH_2 (**8b**)); 1.87–2.05 (m, 1.65H, CH_2 (**8a**))*; 2.12–2.25 (m, 0.9H, CH_2 (**8b**)); 2.40 (ddd, $^2J_{HH}$ 14.5, $^3J_{HH}$ 6.9, $^2J_{PH}$ 4.3, 0.45H, CH_2 (**8b**)); 2.45 (ddd, $^2J_{HH}$ 14.5, 3JHH 5.8, $^2J_{PH}$ 1.5, 0.55H, CH_2 (**8a**)); 3.18 (s, 1.65H, CH_3 (**8a**)); 3.19 (s, 1.35H, CH_3 (**8b**)); 3.25 (s, 1.35H, CH_3 (**8b**)); 3.30 (s, 1.65H, CH_3 (**8a**)); 3.56–3.71 (m, 2H, CH); 7.15–7.52 (m, 20H, phenyl-H)*. $^1H\{^{31}P\}$-NMR: 1.93, 1.95 (AB-part of an ABX-system, $^2J_{AB}$ 14.7, 1.1H, CH_2 (**8a**)); 2.02 (dd, $^2J_{HH}$ 14.5, $^3J_{HH}$ 8.2, 0.55H, CH_2 (**8a**)). ^{31}P-NMR ($CDCl_3$): δ (ppm) 34 (br, phenyl-tarpholane-P); 60 (br, PPh_3).

4.8.1. Separation of the diastereomers

Recrystallization of a sample **8a**:**8b** = 55:45 from ether afforded red crystals with a molar ratio **8a**:**8b** = 74:26.

4.9. Co(CO)(NO)(PPh$_2$Me)(phenyl-tarpholane) *9a*, *9b*

A mixture of Co(CO)(NO)(PPh$_2$Me)$_2$ (0.90 g, 1.74 mmol) and (*R*,*R*)-(+)-phenyl-tarpholane (0.39 g, 1.74 mmol) in 20 ml of toluene was refluxed for 5 h. Chromatography on silica with toluene/petroleum ether 40–60 3:1 afforded two bands. The first one provided the remaining Co(CO)(NO)(PPh$_2$Me)$_2$. The second band was chromatographed a second time with ether/petroleum ether 40–60 2:3. By this procedure the by-product Co(CO)(NO)(phenyl-tarpholane)$_2$ could be separated and the diastereomers **9a**, **9b** were obtained as a red solid after removal of the solvent. Yield: 310 mg (33%), molar ratio **9a**:**9b** = 50:50, m.p. 73–74°C. $[\alpha]_D^{22} = +50$ (c 0.976, CH_2Cl_2). ^1H-NMR (C_6D_6): δ (ppm, J (Hz)) 1.44–1.46 (2 d, $^2J_{PH}$ 6.6, 3H, PCH_3); 1.81–2.01 (m, 1.5H, CH_2); 2.12–2.21 (m, 1H, CH_2); 2.29–2.45 (m, 1.5H, CH_2); 2.80 (s, 1.5H, OCH_3); 2.84 (s, 1.5H, OCH_3); 3.00 (s, 1.5H, OCH_3); 3.05 (s, 1.5H, OCH_3); 3.60–3.72 (m, 2H, CH); 6.93–7.04 (m, 9H, phenyl-H); 7.35–7.51 (m, 6H, phenyl-H). ^{31}P-NMR (C_6D_6): δ (ppm) 39 (br, phenyl-tarpholane-P and PPh_2Me).

4.10. X-ray structure analysis of the complexes *1*, *2a*, *3b*, *4*, *7* and *8a*

X-ray diffraction data were collected with a Syntex-Nicolet R3 diffractometer (**2a** and **8a**; $T = 20$°C) or with a Siemens Stoe AED II diffractometer (**1**; $T = 20$°C; **3b**; $T = -70$°C; **4** and **7**; $T = -80$°C). Mo-K$_\alpha$ radiation ($\lambda = 0.71069$ Å) and a graphite-crystal monochromator were used. Data were collected by the ω-scan technique. The absorption correction was done by empirical methods and the structures were solved using direct methods with SHELXTL PLUS Release 4.2/800 (exceptions: **3b**, direct methods were used with

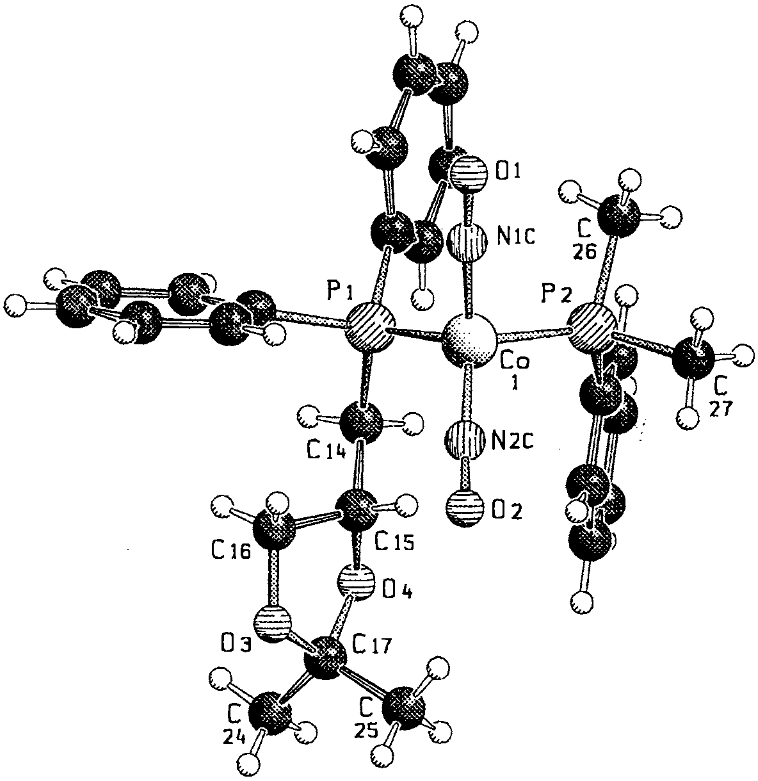


Fig. 5. SCHAKAL view of the molecular structure of Co(CO)(NO)(PMe_2Ph)[(*R*)-glyphos] **7**. Only selected labels are shown for clarity.

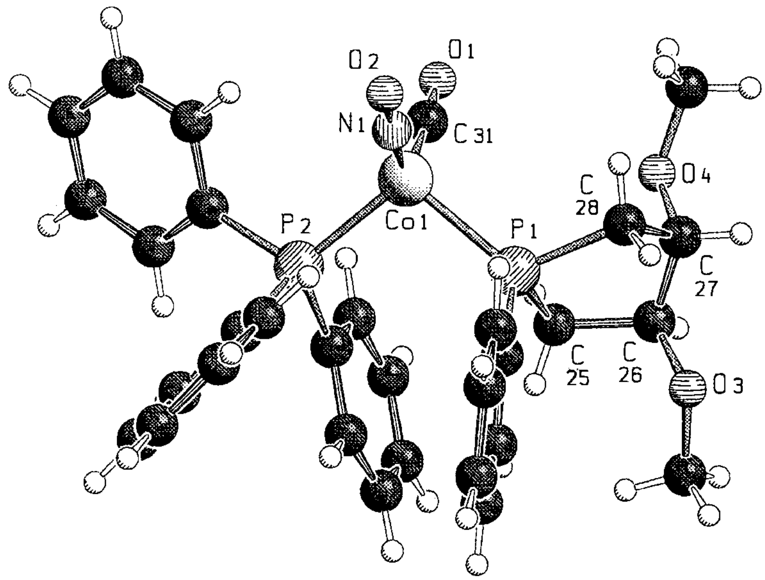


Fig. 6. SCHAKAL view of the molecular structure of (S_{Co},R_C,R_C)-Co(CO)(NO)(PPh_3)(phenyl-tarpholane) **8a**. Only selected labels are shown for clarity.

SHELXL-93; **1** and **2a**, here the Patterson–Fourier method was used with SHELXTL PLUS Release 4.11/V) [18]. The hydrogen atoms were calculated by the option HFIX of the program packages. Further details of the structure determinations have been deposited at the Fachinformationszentrum Karlsruhe, 76344 Eggenstein–Leopoldshafen with the following numbers: CSD 407511 (**1**); CSD 407510 (**2a**); CSD 407508 (**3b**); CSD 407512 (**4**); CSD 407509 (**7**); CSD 407513 (**8a**).

Acknowledgements

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Table 3
Selected bond lengths [Å] of the complexes **1**, **2a**, **3b**, **4**, **7** and **8a**

Complex	**1**[a]	**2a**	**3b**[b]	**4**[a]	**7**[a]	**8a**
Co–C(CO)	1.713(10)	1.633(39)	1.717(6)/1.669(7)	1.725(5)	1.709(4)	1.706(14)
C–O	1.126(13)	1.189(54)	1.156(8)/1.171(9)	1.151(6)	1.156(5)	1.150(17)
Co–N(NO)	1.703(12)	1.629(32)	1.696(7)/1.703(6)	1.725(5)	1.686(3)	1.640(13)
N–O	1.147(15)	1.205(42)	1.158(8)/1.162(8)	1.151(6)	1.159(4)	1.186(18)
Co–C(CN)	—	2.003(43)	1.860(6)/1.862(7)	—	—	—
C–N	—	1.143(57)	1.155(7)/1.165(8)	—	—	—
(CN)N–C	—	1.373(56)	1.455(6)/1.454(7)	—	—	—
Co–P	2.149(4)	2.218(8)	2.207(2)/2.211(2)	—	2.213(1)	2.208(2)
Co–P*[c]	2.224(4)	—	—	2.208(2)	2.207(1)	2.201(2)

[a] No distinction could be made between CO and NO groups.
[b] Two independent molecules per unit cell.
[c] P* stands for the optically active phosphane ligand.

Table 4
Selected bond angles [°] of the complexes **1**, **2a**, **3b**, **4**, **7** and **8a**

Complex	**1**[a]	**2a**	**3b**[b]	**4**[a]	**7**[a]	**8a**
Co–C–O	177.2(11)	175.0(37)	175.1(6)/175.6(6)	177.5(5)	177.9(3)	176.7(10)
Co–N–O	174.8(11)	171.8(21)	178.5(6)/174.8(8)	177.5(5)	177.4(3)	177.7(9)
C(CO)–Co–N(NO)	121.6(5)	118.3(21)	123.3(3)/121.8(3)	124.3(3)	123.3(2)	122.4(5)
Co–C–N	—	176.0(28)	179.4(5)/172.8(6)	—	—	—
C–N–C	—	175.3(29)	171.7(5)/172.4(6)	—	—	—
C(CO)–Co–C(CN)	—	110.4(17)	108.6(3)/112.1(3)	—	—	—
N(NO)–Co–C(CN)	—	110.0(15)	113.5(3)/112.2(3)	—	—	—
C(CO)–Co–P	107.9(4)	104.8(11)	97.9(2)/94.6(2)	—	101.7(1)	101.8(3)
N(NO)–Co–P	106.6(4)	111.7(11)	108.2(2)/105.1(2)	—	110.6(1)	115.9(3)
C(CN)–Co–P	—	100.0(10)	101.5(2)/107.2(2)	—	—	—
C(CO)–Co–P*	103.4(4)	—	—	103.9(2)	105.7(1)	104.0(4)
N(NO)–Co–P*	111.8(4)	—	—	110.0(2)	112.8(1)	109.0(3)
P–Co–P*	104.2(1)	—	—	—	99.7(1)	101.3(1)
P*–Co–P*	—	—	—	103.0(1)	—	—

[a–c] See Table 3.

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