

# Optically active transition metal compounds 112<sup>1</sup>. Synthesis of chiral carbonylnitrosylcobalt complexes with bidentate PP\*, PN\* and NN\* ligands<sup>2</sup>

Henri Brunner<sup>a,\*</sup>, Peter Faustmann<sup>a</sup>, Andreas Dietl<sup>a</sup>, Bernhard Nuber<sup>b</sup>

<sup>a</sup> *Institut für Anorganische Chemie der Universität Regensburg, 93040 Regensburg, Germany*

<sup>b</sup> *Anorganisch-Chemisches Institut der Universität Heidelberg, 69120 Heidelberg, Germany*

Received 13 December 1996

## Abstract

The substitution of two carbonyl groups in  $\text{Co}(\text{CO})_3(\text{NO})$  by optically active unsymmetrical bidentate ligands  $\text{LL}^*$  yields pairs of diastereomers  $\text{Co}(\text{CO})(\text{NO})(\text{LL}^*)$ , which differ only in the configuration at the Co atom.  $\text{LL}^*$  can be a bisphosphane, trisphosphane, phosphaneimine or pyridineimine. For the complexes **2** ( $\text{LL}^* = (\text{S,S})\text{-norphos}$ ), **3** ( $\text{LL}^* = (\text{R})\text{-1,2,4-triphos}$ ) and **4** ( $\text{LL}^* = (\text{R})\text{-1,2,5-triphos}$ ) the diastereomer ratios of 45:55 (**2a:2b**), 83:17 (**3a:3b**) and 63:37 (**4a:4b**) respectively indicate an optical induction from the ligand to the metal configuration during the synthesis. By crystallization it is possible to separate the diastereomers of **1** ( $\text{LL}^* = (\text{R})\text{-prophos}$ ), **2** and **3**. **1a** and **3a** are obtained as pure diastereomers, **2a** as an enriched sample (**2a:2b** 73:27). The crystal structures and absolute configurations of  $(S_C, R_C)\text{-1a}$  and  $(S_C, R_C)\text{-3a}$  were determined by X-ray analysis. In **3a** the cobalt center is configurationally stable at room temperature, whereas **1a** epimerizes in benzene-*d*<sub>6</sub> at 35°C with a half-life of  $\tau_{1/2} = 141$  min and **2a** in  $\text{CDCl}_3$  at 24°C with  $\tau_{1/2} = 160$  min. © 1997 Elsevier Science S.A.

**Keywords:** Chirality; Cobalt(carbonyl)(nitrosyl) complexes; X-ray structure analysis

## 1. Introduction

In the investigation of the stereochemical course of reactions optically active organometallic complexes have become more and more important since the first example was reported [2]. Most of these complexes are of the type  $(\eta^5\text{-C}_5\text{H}_5)\text{MABC}$  or  $(\eta^6\text{-arene})\text{MABC}$ , i.e. they have pseudo-octahedral geometry [3–6]. Purely tetrahedral chiral complexes are rare. Diastereomeric complexes of the type  $\text{Fe}(\text{CO})(\text{NO})(\text{NNAr})(\text{PPh}_2\text{NRR}^*)$  [7] have been separated. As in  $\text{Co}(\text{CO})_3(\text{NO})$ , two carbonyl groups are substitutionally labile,  $\text{Co}(\text{CO})(\text{NO})(\text{LL}^*)$  is a good candidate for tetrahedral complexes chiral at the metal atom. The isolation of the racemates of  $\text{Co}(\text{CO})(\text{NO})(\text{PPh}_3)(\text{AsPh}_3)$  and  $\text{K}[\text{Co}(\text{CO})(\text{NO})(\text{CN})(\text{PPhR}_2)]$  [8,9] and of the mixture of diastereomers of  $\text{Co}(\text{CO})(\text{NO})(\text{PPh}_3)(\text{L}^*)$  ( $\text{L}^* =$  optically active carbene) [10–12] has been described.

We report herein the synthesis of new complexes of the type  $\text{Co}(\text{CO})(\text{NO})(\text{LL}^*)$ , in which the unsymmetrical ligand  $\text{LL}^*$  is an optically active bisphosphane, trisphosphane, phosphaneimine or pyridineimine. The complexes are formed as pairs of diastereomers which differ only in the configuration at the cobalt center. For two of these complexes separation of the diastereomers has been possible by repeated crystallization. We were able to determine their absolute configurations by X-ray structure analysis.

## 2. Results and discussion

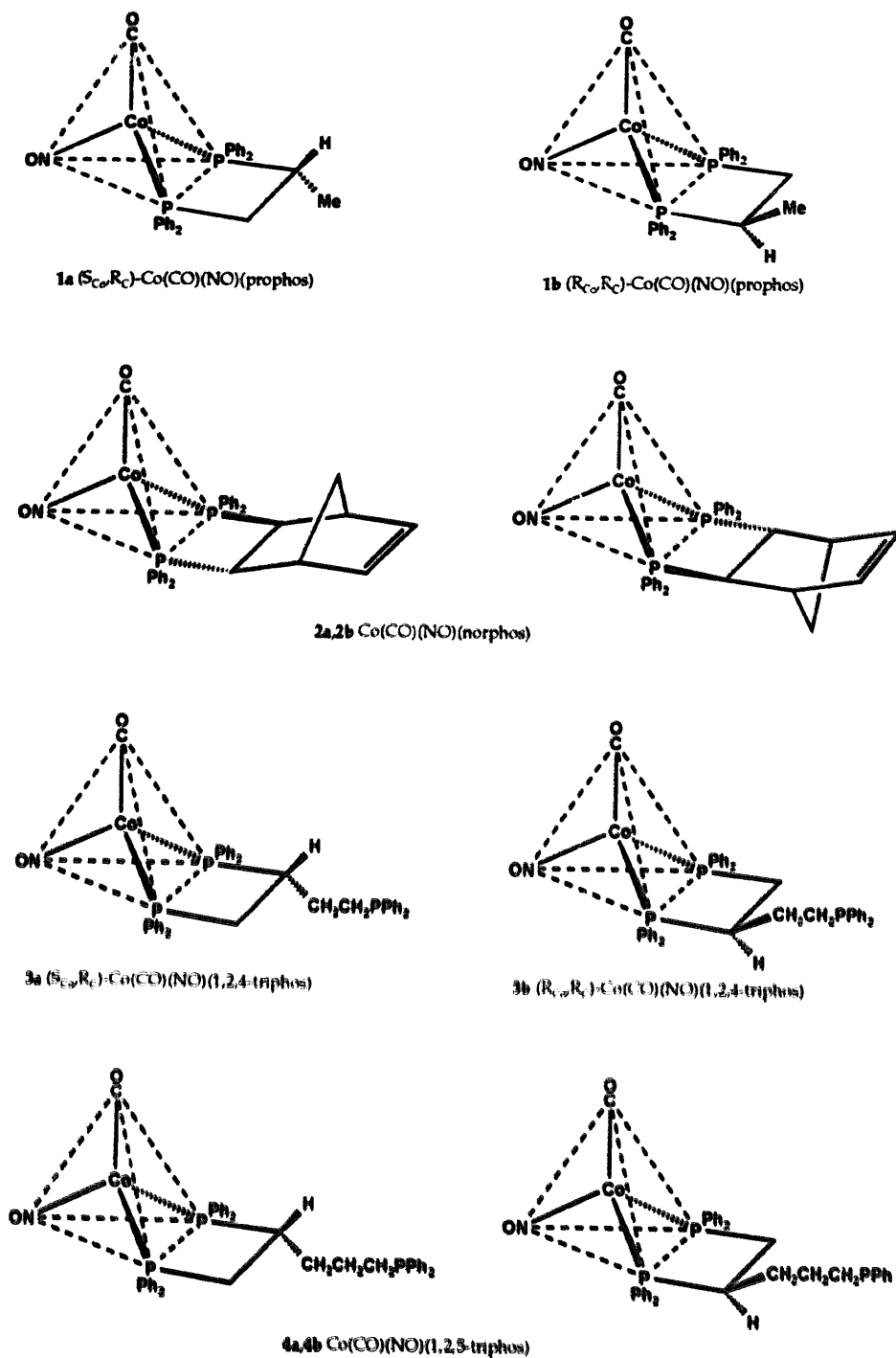
All the complexes were synthesized by reaction between  $\text{Co}(\text{CO})_3(\text{NO})$  and the free ligand at an appropriate temperature (Schemes 1 and 2).

Usually a small excess of  $\text{Co}(\text{CO})_3(\text{NO})$  was used, with the exception of the reactions with the trisphosphanes. In these cases less than one equivalent of  $\text{Co}(\text{CO})_3(\text{NO})$  was employed in order to avoid complexation of all three phosphorus atoms. All the reactions were monitored by IR spectroscopy. After completion

\* Corresponding author.

<sup>1</sup> For Part 111 see Ref. [1].

<sup>2</sup> Dedicated to Professor Wolfgang Beck on the occasion of his 65th birthday.

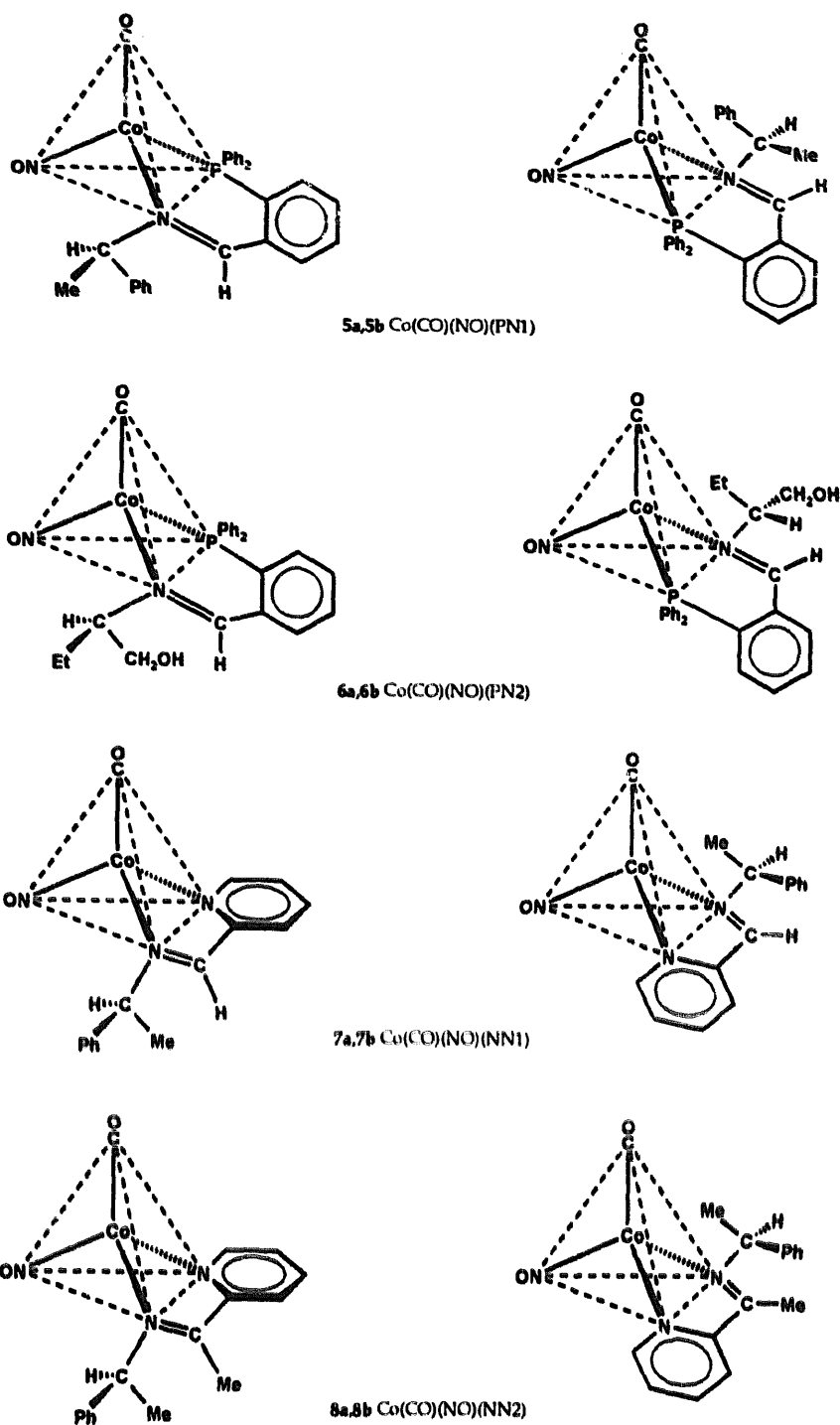


Scheme 1.

of the reactions the products were purified by chromatography, in most cases on silica. In Table 1 the analytical, IR and FD MS data for the complexes 1–8 are summarized.

Whilst the complexes with the bis- and triphosphanes are, even in solution, relatively air-stable, the complexes with the ligands containing a nitrogen donor are very air-sensitive. For the pyridine/imine complexes the use of an argon atmosphere was necessary, as they are extremely sensitive to oxygen.

The IR spectra of all the complexes 1–8 exhibit only one carbonyl band. This proves the substitution of two carbonyl groups in  $\text{Co(CO)}_3(\text{NO})$  and therefore indicates (together with the FD mass spectra) that all the ligands form chelate rings. The wavenumbers of both carbonyl and nitrosyl bands are lower the weaker the  $\pi$ -acceptor properties of the ligands, i.e. the more nitrogen donors are present. The values of  $1910$  and  $1920\text{ cm}^{-1}$  for the carbonyl group and  $1660\text{ cm}^{-1}$  for the nitrosyl group in the complexes 7 and 8 with  $\text{NN}^+$



Scheme 2.

ligands are in good agreement with the values found for other Co(CO)(NO)(NN) complexes [8]. Also the values for the complexes with PP\* ligands (carbonyl frequencies in the range 1950–1960 cm<sup>-1</sup>, nitrosyl frequencies in the range 1690–1700 cm<sup>-1</sup>) are in accord with similar complexes [8,13–15]. For the PN\* ligands, however, no such comparison can be made as there are no similar complexes, though attempts for their synthesis have been reported [16]. The values we found for **5** and

**6** (1920 and 1690 cm<sup>-1</sup>, 1930 and 1680 cm<sup>-1</sup> respectively) are intermediate between those for the NN\* and PP\* complexes, as expected.

The use of the optically pure ligands in the synthesis of the complexes **1–8** leads to pairs of diastereomers **a/b**, which only differ in the configuration at the cobalt atom. The ratio of the diastereomers can be determined by <sup>1</sup>H NMR spectroscopy, as there is at least one set of signals in which each pair of diastereomers can be

Table 1  
IR spectroscopic, analytical and FD MS data for the carbonyl nitrosyl cobalt complexes 1–8

Co(CO)(NO)(LL') LL' =	IR [cm <sup>-1</sup> ] <sup>a</sup>		Analyses			FD MS [e/m] <sup>c</sup> (M <sup>+</sup> ) <sup>d</sup>	Formula
	$\nu(\text{CO})$	$\nu(\text{NO})$	C	H	N		
1 Prophos	1950	1690	63.70 (63.52)	4.97 (4.95)	2.77 (2.65)	529.4 (529.40)	C <sub>28</sub> H <sub>26</sub> CoNO <sub>2</sub> P <sub>2</sub>
2 Norphos	1950	1700	66.18 (66.40)	4.84 (4.88)	2.57 (2.42)	578.8 (579.46)	C <sub>32</sub> H <sub>28</sub> CoNO <sub>2</sub> P <sub>2</sub>
3 1,2,4-Triphos	1961	1693	67.60 (67.68)	5.14 (5.13)	1.90 (1.93)	699.1 <sup>e</sup> (727.61)	C <sub>41</sub> H <sub>37</sub> CoNO <sub>2</sub> P <sub>3</sub>
4 1,2,5-Triphos	1950	1698	67.45 (68.02)	5.27 (5.30)	1.91 (1.89)	713.2 <sup>e</sup> (741.64)	C <sub>28</sub> H <sub>39</sub> CoNO <sub>2</sub> P <sub>3</sub>
5 PN1	1920	1690	65.71 (65.89)	4.65 (4.74)	5.41 (5.49)	510.2 (510.42)	C <sub>28</sub> H <sub>24</sub> CoN <sub>2</sub> O <sub>2</sub> P
6 PN2	1930	1680	60.13 (60.38)	4.87 (4.86)	5.67 (5.87)	478.2 (477.37)	C <sub>24</sub> H <sub>23</sub> CoN <sub>2</sub> O <sub>3</sub> P
7 NN1	1920	1660	54.59 (55.06)	4.17 (4.31)	12.52 (12.84)	326.9 (327.23)	C <sub>15</sub> H <sub>14</sub> CoN <sub>3</sub> O <sub>2</sub>
8 NN2	1910	1660	55.82 (56.32)	4.85 (4.73)	11.88 (12.32)	341.2 (341.26)	C <sub>16</sub> H <sub>16</sub> CoN <sub>3</sub> O <sub>2</sub>

<sup>a</sup> KBr pellets, strong absorptions.

<sup>b</sup> Calculated values in parentheses.

<sup>c</sup> Solvent toluene.

<sup>d</sup> Calculated M in parentheses.

<sup>e</sup> M<sup>+</sup> was not detected, the value given is M<sup>+</sup> – CO.

differentiated. After work-up the diastereomer ratio for complexes 1, 5, 6, 7, and 8 is 50:50. Only for complexes 2, 3, and 4 does the ratio differ from 50:50, indicating an optical induction from the ligand to the

metal atom during the synthesis. These ratios are 2a:2b 45:55, 3a:3b 83:17, and 4a:4b 63:37. In order to separate the diastereomers we tested chromatographic methods as well as crystallization. With 1, 2, and 3 the latter

Table 2  
Summary of crystal data, data collection and structure refinement for 1a and 3a

Crystal parameters	1a	3a
Complex	1a	3a
Formula	C <sub>28</sub> H <sub>26</sub> CoNO <sub>2</sub> P <sub>2</sub>	C <sub>41</sub> H <sub>37</sub> CoNO <sub>2</sub> P <sub>3</sub>
Mol. wt.	529.40	727.61
Color and shape	dark red, pyramidal	dark red, irregular
Size [mm <sup>3</sup> ]	0.30 × 0.75 × 0.75	0.30 × 0.35 × 0.40
Crystal system	monoclinic	rhombic
Space group	<i>P</i> 2 <sub>1</sub> (4)	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (19)
<i>a</i> [Å]	9.770(5)	10.438(6)
<i>b</i> [Å]	13.214(5)	17.670(9)
<i>c</i> [Å]	10.398(4)	19.73(1)
$\alpha$ [deg]	90	90
$\beta$ [deg]	108.06(2)	90
$\gamma$ [deg]	90	90
<i>V</i> [Å <sup>3</sup> ]	1276.3	3639.0
<i>Z</i>	2	4
<i>D</i> <sub>calc</sub> [g cm <sup>-3</sup> ]	1.38	1.33
<i>F</i> (000)	548	1512
$\mu$ [mm <sup>-1</sup> ]	0.82	0.64
Data collection		
<i>hkl</i> ranges	0–14; –19–19; –15–15	0–14; 0–24; 0–27
2 $\theta$ range [deg]	3.0–60.0	3.0–58.0 <sup>a</sup>
Total no. of unique reflections	7458	6801
No. of observed reflections ( <i>I</i> > 2.5 $\sigma$ ( <i>I</i> ))	5996	4359
Min.; max. transmission factors	0.83; 1.00	0.84; 1.00
Data refinement		
No. of reflections and 2 $\theta$ range [deg] for empirical absorption correction	7; 11.0–45.0	6; 8.0–29.0
No. of LS parameters	307	433
Largest shift/e.s.d. in final cycle	0.010	0.025
$\Delta\rho_{\text{min}}$ ; $\Delta\rho_{\text{max}}$ [e Å <sup>-3</sup> ]	–0.78; 0.91	–0.41; 0.49
<i>R</i> <sup>b</sup> ; <i>R</i> <sub>w</sub> <sup>c</sup>	0.044; 0.036	0.043; 0.031

<sup>a</sup> Friedel pairs measured between 3° and 40°; *h*: 1–10; *k*: 1–17; *l*: –19–(–1).

<sup>b</sup>  $R = \sum ||F_o - F_c| / |F_o|$ .

<sup>c</sup>  $R_w = \sum ||F_o - F_c| w^{1/2} / \sum |F_o| w^{1/2}$ ,  $w = 1/\sigma^2(F_o)$ .

method was successful. **1a** and **3a** were obtained as pure diastereomers, **2a** in an enriched sample (ratio **2a:2b** 73:27).

There are three ways in which trisphosphane ligands may coordinate to the cobalt atom. With 1,2,4-triphos a five-, six- or seven-membered ring and with 1,2,5-triphos a five-, seven- or eight-membered ring is possible. However, the complexation is highly selective:  $^{31}\text{P}$  NMR spectroscopy shows that in the former case the five-membered ring compound is the only product. There are only two broad resonances for the coordinated C1–P and C2–P (66.8 and 87.0 ppm) and two singlets for the uncoordinated C4–P phosphorus atoms (–18.00 ppm for **3a** and –17.58 ppm for **3b**). In the latter case the five-membered ring compound is the main product: the broad resonances at 68.6 and 87.2 ppm belong to the coordinated phosphorus atoms C1–P and C2–P, the singlets at –15.63 and –15.57 ppm to the uncoordinated C5–P atoms (diastereomers **4b** and **4a**). The small doublets at –19.59 and –20.34 ppm in the spectrum of **4** may be attributed to ring isomers.

Whilst in **3a**, in solution, the cobalt center is configu-

Table 3  
Atomic coordinates of **1a**

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Co	0.2056(1)	0.0000	0.1347(1)
P1	0.1154(1)	0.0669(1)	–0.0683(1)
P2	0.3108(1)	0.1467(1)	0.2045(1)
O1	0.0081(3)	–0.0911(2)	0.2482(3)
O2	0.4505(3)	–0.1151(2)	0.1104(3)
N1	0.0919(3)	–0.0509(2)	0.2035(3)
C1	–0.1686(3)	0.0446(3)	–0.0741(3)
C2	–0.3150(4)	0.0627(3)	–0.1226(4)
C3	–0.3700(4)	0.1277(3)	–0.2292(5)
C4	–0.2813(4)	0.1726(3)	–0.2870(4)
C5	–0.1356(3)	0.1550(3)	–0.2418(4)
C6	–0.0774(3)	0.0905(2)	–0.1336(3)
C7	0.0463(3)	–0.0361(3)	–0.3187(3)
C8	0.0812(4)	–0.0840(3)	–0.4225(3)
C9	0.2230(4)	–0.0896(3)	–0.4214(4)
C10	0.3296(4)	–0.0477(3)	–0.3145(4)
C11	0.2951(3)	–0.0019(3)	–0.2108(3)
C12	0.1524(3)	0.0061(3)	–0.2113(3)
C13	0.2160(3)	0.1620(3)	0.4299(3)
C14	0.2051(4)	0.2054(3)	0.5468(4)
C15	0.2818(4)	0.2910(3)	0.5972(4)
C16	0.3705(5)	0.3308(3)	0.5323(4)
C17	0.3814(4)	0.2876(3)	0.4159(4)
C18	0.3026(3)	0.2029(2)	0.3621(3)
C19	0.5600(3)	0.2110(3)	0.1412(3)
C20	0.7064(4)	0.2119(3)	0.1615(4)
C21	0.7962(4)	0.1567(4)	0.2636(5)
C22	0.7400(4)	0.1017(3)	0.3455(4)
C23	0.5945(4)	0.1013(3)	0.3264(4)
C24	0.5017(3)	0.1563(2)	0.2240(3)
C25	0.2208(3)	0.2420(2)	0.0748(3)
C26	0.1972(3)	0.1938(2)	–0.0632(3)
C27	0.0783(3)	0.2752(3)	0.0955(3)
C28	0.3537(4)	–0.0696(3)	0.1187(3)

Table 4  
Atomic coordinates of **3a**

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Co	0.3121(1)	0.0182(1)	0.2269(1)
P1	0.3969(1)	0.0040(1)	0.1258(1)
P2	0.2258(1)	–0.2709(1)	0.0458(1)
P3	0.3173(1)	–0.1060(1)	0.2389(1)
O1	0.4380(4)	0.1109(2)	0.3231(2)
O2	0.0532(3)	0.0525(2)	0.1810(2)
N1	0.3859(4)	0.0713(2)	0.2838(2)
C1	0.6244(4)	0.0815(2)	0.1512(3)
C2	0.7410(5)	0.1137(3)	0.1348(3)
C3	0.7802(5)	0.1163(3)	0.0677(3)
C4	0.7038(5)	0.0860(3)	0.0181(3)
C5	0.5857(5)	0.0541(3)	0.0341(2)
C6	0.5448(4)	0.0513(3)	0.1017(2)
C7	0.2531(5)	0.1004(3)	0.0456(3)
C8	0.1600(5)	0.1208(3)	–0.0006(3)
C9	0.0992(5)	0.0648(4)	–0.0371(3)
C10	0.1301(5)	–0.0089(3)	–0.0276(2)
C11	0.2236(4)	–0.0298(3)	0.0193(2)
C12	0.2860(4)	0.0250(3)	0.0567(2)
C13	0.0200(5)	–0.3577(4)	0.0862(3)
C14	–0.0436(7)	–0.4173(4)	0.1191(3)
C15	0.0226(7)	–0.4646(4)	0.1599(3)
C16	0.1508(6)	–0.4556(3)	0.1690(3)
C17	0.2181(5)	–0.3991(3)	0.1351(3)
C18	0.1524(5)	–0.3491(3)	0.0922(3)
C19	0.2351(4)	–0.2731(3)	–0.0943(2)
C20	0.267(5)	0.3020(3)	–0.1573(3)
C21	0.3256(6)	–0.3718(3)	0.1629(3)
C22	0.3505(6)	–0.4129(3)	–0.1063(3)
C23	0.3200(6)	–0.3854(3)	–0.0430(3)
C24	0.2621(4)	–0.3146(3)	–0.0364(2)
C25	0.5625(4)	–0.1044(3)	0.2960(2)
C26	0.6622(5)	–0.1332(3)	0.3350(2)
C27	0.6487(4)	–0.2004(3)	0.3693(3)
C28	0.5355(5)	–0.2408(3)	0.3651(3)
C29	0.4363(5)	–0.2138(3)	0.3255(3)
C30	0.4492(4)	–0.1449(3)	0.2910(2)
C31	0.1473(4)	–0.1447(3)	0.3407(2)
C32	0.0535(5)	–0.1875(3)	0.3728(3)
C33	–0.0119(5)	–0.2422(3)	0.3366(3)
C34	0.0149(4)	–0.2539(3)	0.2694(3)
C35	0.1098(4)	–0.2117(3)	0.2382(2)
C36	0.1794(4)	–0.1576(2)	0.2731(2)
C37	0.4413(4)	–0.0964(2)	0.1150(2)
C38	0.3457(4)	–0.1487(2)	0.1534(2)
C39	0.3930(4)	–0.2317(2)	0.1535(2)
C40	0.3896(4)	–0.2676(3)	0.0821(2)
C41	0.1548(4)	0.0380(3)	0.2006(2)

rationally stable at room temperature, **1a** and **2a** do epimerize with respect to the cobalt configuration. We measured the rate of the epimerization by  $^1\text{H}$  NMR spectroscopy. The equilibrium ratio of the diastereomers is identical to the ratio found after the preparation of the complexes (**1a:1b** 50:50, **2a:2b** 45:55). Both a 0.03 M solution of pure **1a** and a 0.01 M solution of **2a:2b** in a 73:27 mixture obeyed a first-order rate law (**1a** in benzene- $d_6$  at 35 °C:  $k = 8.22 \times 10^{-5} \text{ s}^{-1}$ ,  $\tau_{1/2} = 141 \text{ min}$ ; **2a** in  $\text{CDCl}_3$  at 24 °C:  $k = 7.32 \times 10^{-5} \text{ s}^{-1}$ ,

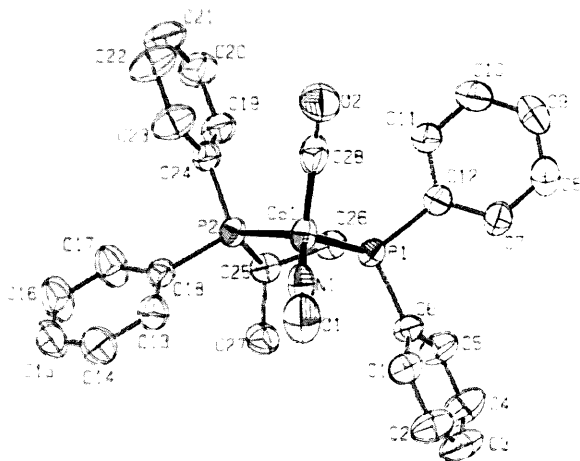


Fig. 1. PLATON view of **1a** showing the labeling scheme used. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids enclose 50% probability levels.

$\tau_{1/2} = 160$  min). The addition of equimolar amounts of (R)-(+)-prophos, dppe or trisisopropylphosphane did not change the rate of epimerization and no products of exchange reactions were detected. Using higher concentrations of the complexes also had no effect on the reaction rate. Measurements of the rate constants at different temperatures allowed us to estimate the activation enthalpy  $\Delta H^\ddagger$  and entropy  $\Delta S^\ddagger$  of the reaction. For both complexes we found  $\Delta H^\ddagger \approx 90 \text{ kJ mol}^{-1}$  and  $\Delta S^\ddagger \approx +20 \text{ k}^{-1} \text{ mol}^{-1}$ . These results indicate that the epimerization is an intramolecular process. However, it is not possible to distinguish between a rearrangement involving an intermediate square planar species and a dissociative mechanism with opening of the chelate ring. Further experiments are underway to elucidate this point.

In the complexes **7** and **8** with  $\text{NN}^+$  ligands the cobalt configuration is more labile than in the com-

plexes with  $\text{PP}^+$  ligands. This was proven by coalescence experiments in  $\text{DMSO-}d_6$ . For **7** a coalescence temperature  $T_c$  of 406 K and for **8** of 413 K was found. The rate constants  $k_{T_c}$  and  $\Delta G^\ddagger$  values were calculated for **7**:  $k_{T_c} = 38.0 \text{ s}^{-1}$ ,  $\Delta G^\ddagger = 87.5 \text{ kJ mol}^{-1}$ , and for **8**:  $k_{T_c} = 51.3 \text{ s}^{-1}$ ,  $\Delta G^\ddagger = 88.1 \text{ kJ mol}^{-1}$ . Extrapolation to room temperature shows that the complexes **7** and **8** epimerize approximately 100 times faster than the complexes **1** and **2**. This explains why we could not separate the diastereomers **7a,7b** and **8a,8b**.

### 3. X-ray structure analysis of **1a** and **3a**

Single crystals for X-ray structure analysis were obtained of the pure diastereomers **1a** and **3a**. Details of both structure determinations have been deposited with the numbers CSD-406185 (**1a**) and CSD-40186 (**3a**) at the Fachinformationszentrum Karlsruhe.

Table 2 gives details of the data collection, structure refinement and crystal data of the complexes **1a** and **3a**. In Tables 3 and 4 the positional parameters are summarized, employing the atom-labeling scheme used in Figs. 1 and 2, and in Tables 5 and 6 selected bond distances and angles are listed.

As expected the coordination geometry of both complexes is a distorted tetrahedron about the cobalt center. Unlike for other complexes of this type, we were able to distinguish the CO and NO groups [10,11]. Therefore we could determine the absolute configuration of both complexes by refinement of the least-squares variable  $\eta$  [17] (for **1a**  $\eta = 1.06(2)$  and for **3a**  $\eta = 0.89(3)$ ). **1a** and also **3a** are assigned  $S_{C_{2v}}, R_C$ -configuration. The Co–N(NO) distances in **1a** (1.641 Å) and **3a** (1.653 Å) as well as the Co–C(CO) distances (1.766 Å and 1.757 Å respectively) lie in the normal range found for other

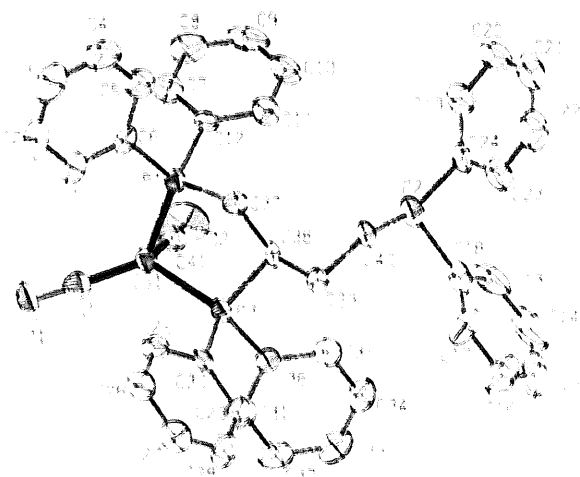


Fig. 2. PLATON view of **3a** showing the labeling scheme used. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids enclose 50% probability levels.

Table 5  
Selected bond lengths [Å] and angles [deg] of **1a** with estimated standard deviations in parentheses

Co–P1	2.204(1)	P1–C12	1.823(3)
Co–P2	2.209(1)	P1–C26	1.852(3)
Co–N1	1.641(3)	P2–C18	1.823(3)
Co–C28	1.766(4)	P2–C24	1.817(3)
N1–O1	1.184(5)	P2–C25	1.855(3)
C28–O2	1.146(5)	C25–C26	1.521(4)
P1–C6	1.820(3)	C25–C27	1.537(5)
P1–Co–P2	88.3(0)	Co–P1–C26	107.2(1)
P1–Co–N1	117.3(1)	Co–P2–C18	120.5(1)
P1–Co–C28	102.4(1)	Co–P2–C24	117.0(1)
P2–Co–N1	121.7(1)	Co–P2–C25	106.8(1)
P2–Co–C28	100.2(1)	C6–P1–C12	102.4(1)
N1–Co–C28	120.9(2)	C6–P1–C26	104.0(1)
Co–N1–O1	176.8(3)	C12–P1–C26	103.2(2)
Co–C28–O2	179.0(3)	C18–P2–C24	101.6(1)
Co–P1–C6	119.1(1)	C18–P2–C25	103.5(1)
Co–P1–C12	118.9(1)	C24–P2–C25	105.8(1)

Table 6  
Selected bond lengths [Å] and angles [deg] of **3a** with estimated standard deviations in parentheses.

Co–P1	2.197(2)	P2–C18	1.826(5)
Co–P3	2.210(2)	P2–C24	1.835(5)
Co–N1	1.653(4)	P2–C40	1.855(4)
Co–C41	1.757(5)	P3–C30	1.850(5)
N1–O1	1.177(6)	P3–C36	1.832(5)
C41–O2	1.158(6)	P3–C38	1.871(4)
P1–C6	1.819(5)	C37–C38	1.557(6)
P1–C12	1.826(4)	C38–C39	1.548(6)
P1–C37	1.845(4)	C39–C40	1.546(6)
P1–Co–P3	88.5(1)	Co–P3–C36	121.0(1)
P1–Co–N1	119.6(1)	Co–P3–C38	107.9(1)
P1–Co–C41	97.6(1)	C6–P1–C12	104.4(2)
P3–Co–N1	118.7(1)	C6–P1–C37	101.4(2)
P3–Co–C41	104.6(2)	C12–P1–C37	105.6(2)
N1–Co–C41	121.5(2)	C18–P2–C24	102.2(2)
Co–N1–O1	178.0(4)	C18–P2–C40	102.5(2)
Co–C41–O2	177.2(4)	C24–P2–C40	99.4(2)
Co–P1–C6	121.8(2)	C30–P3–C36	101.2(2)
Co–P1–C12	113.5(1)	C30–P3–C38	103.5(2)
Co–P1–C37	108.4(1)	C36–P3–C38	104.9(2)
Co–P3–C30	116.5(2)		

Co(CO)(NO) complexes [10,15,18]. The same holds for the N–O and C–O distances (1.184 Å and 1.146 Å in **1a**, 1.177 Å and 1.158 Å in **3a**). The NO and CO groups are found to be nearly linear (angles range from 176.8° to 179.0°) in accord with known complexes. Also all the Co–P distances in **1a** and **3a** have normal values (2.204 Å and 2.209 Å in **1a**, 2.197 Å and 2.210 Å in **3a**). As in both complexes the ligand forms a five-membered ring with the Co center, the angles P–Co–P are much smaller (88.30 in **1a**, 88.50 in **3a**) than in Co(CO)(NO) complexes with four unidentate ligands [10,15,18], but they are within the normal range for this kind of metallacycle [19]. **1a** deviates remarkably from expectation: the methyl group of the prophos ligand is not in an equatorial but in an axial position of the five-membered ring [20]. In **3a**, however, the CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub> group is in the expected equatorial position.

#### 4. Experimental

All the complexes were prepared under an atmosphere of dried nitrogen (complexes **1–6**) or argon (complexes **7** and **8**). 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. <sup>1</sup>H and <sup>31</sup>P NMR spectra were obtained on a Bruker AC 250 and a Bruker ARX 400 spectrometer [250.13 or 400.13 MHz (<sup>1</sup>H) and 161.98 MHz (<sup>31</sup>P)]. Chemical shifts are in ppm downfield from TMS or 85% H<sub>3</sub>PO<sub>4</sub> 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.

Literature methods were used to prepare the eight ligands as indicated in the individual procedures. Co(CO)<sub>3</sub>(NO) was prepared by the method of Hieber et al. [21], it was stored under nitrogen at –25 °C and not purified further prior to use.

#### 4.1. General procedure for synthesis of the complexes **1–8**

At 0 °C the required amount of Co(CO)<sub>3</sub>(NO) was dissolved in toluene or THF respectively. After addition of the ligand the solution was slowly warmed up to the appropriate temperature and kept at this temperature until the reaction was complete. During this time the color of the solution turned from orange to dark red or brown. Then the solution was concentrated and filtered or chromatographed to remove decomposition products. From the resulting solution the solvent was evaporated and the residue was recrystallized if necessary.

#### 4.2. Co(CO)(NO)(prophos) **1a,1b**

A mixture of Co(CO)<sub>3</sub>(NO) (0.70 g, 4.0 mmol) and (R)-(+)–1,2-bis(diphenylphosphanyl)propane (prophos) [22] (1.48 g, 3.6 mmol) was refluxed in 20 ml of toluene for 16 h. The crude product was purified by chromatography on Sephadex LH-20 with CH<sub>2</sub>Cl<sub>2</sub>. After evaporating the solvent a red powder was obtained. Yield 1.16 g (62%); molar ratio **1a**:**1b** 50:50. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.70 (dd, <sup>3</sup>J(CH<sub>3</sub>–CH) = 7.1 Hz, <sup>3</sup>J(CH<sub>3</sub>–P) = 12.0 Hz, 3H, CH<sub>3</sub> (**1b**)), 0.93 (dd, <sup>3</sup>J(CH<sub>3</sub>–CH) = 7.1 Hz, <sup>3</sup>J(CH<sub>3</sub>–P) = 12.0 Hz, 3H, CH<sub>3</sub> (**1a**)), 2.14–2.61 (m, 5H, CH<sub>2</sub>–CH (**1a**) and CH<sub>2</sub> (**1b**)), 2.78–3.01 (m, 1H, CH (**1b**)), 7.24–7.85 (m, 40H, phenyl-H). <sup>31</sup>P NMR (toluene-*d*<sub>8</sub>): δ 65.6 (br, 1P (**1b**)), 69.9 (br, 1P (**1a**)), 86.7 (br, 2P (**1a**) and (**1b**)).

##### 4.2.1. Separation of the diastereomers

At –18 °C pentane was condensed into a solution of 3.0 g of **1a**:**1b** 50:50 in 20 ml of toluene. After several days red crystals formed. With these crystals the procedure was repeated five times. Finally the pure diastereomer **1a** was obtained as crystals suitable for X-ray analysis. Yield 350 mg (12%), m.p. 197–198 °C. [ $\alpha$ ]<sub>D</sub><sup>25</sup> = –38 (c 1, toluene).

#### 4.3. Co(CO)(NO)(norphos) **2a,2b**

After refluxing a mixture of Co(CO)<sub>3</sub>(NO) (0.80 g, 4.6 mmol) and (S,S)-(+)–5,6-bis(diphenylphosphanyl)bicyclo[2.2.1]hept-2-ene (norphos) [23,24] (2.0 g, 4.3 mmol) in 20 ml of toluene for 16 h the solution was filtered over a small amount of silica. The

solvent was removed to provide **2a,2b** as a reddish brown solid. Yield 1.97 g (78%), molar ratio **2a:2b** 45:55.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.74–3.09 (m, 6H, aliph. H), 5.13 (dd,  $^3J = 5.5$  Hz,  $^3J = 2.6$  Hz, 0.55H, =CH (**2b**)), 5.20 (dd,  $^3J = 5.5$  Hz,  $^3J = 2.6$  Hz, 0.45H, =CH (**2a**)), 6.04–6.09 (m, 1H, =CH), 7.15–7.81 (m, 20H, phenyl-H).  $^{31}\text{P}$  NMR (toluene- $d_8$ ):  $\delta$  47.4 (br, 1P (**2b**)), 48.7 (br, 1P (**2a**)), 53.7 (br, 2P (**2a**) and (**2b**)).

#### 4.3.1. Separation of the diastereomers

The same procedure as described above for **1a** was followed. Red brown crystals were obtained containing **2a:2b** in a molar ratio of 73:27, m.p. 182–184°C.  $[\alpha]_D^{25} = -47$  (c 1, toluene).

#### 4.4. $\text{Co}(\text{CO})(\text{NO})(1,2,4\text{-triphos})$ **3a,3b**

A mixture of  $\text{Co}(\text{CO})_3(\text{NO})$  (1.1 g, 6.4 mmol) and (R)-(+)-1,2,4-tris(diphenylphosphanyl)butane (1,2,4-triphos) [25] (4.0 g, 6.5 mmol) in 40 ml of THF was refluxed for 3 h. After removal of the solvent, the residue was chromatographed on silica. Elution with THF:petroleum ether 40–60 (1:1) gave an orange band. Evaporating the solvent afforded **3a,3b** as an orange powder. Yield 4.4 g (95%), molar ratio **3a:3b** 83:17.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.74–0.89 (m, 0.17H,  $\text{C}_3\text{H}_2$  (**3b**)), 1.08–1.20 (m, 0.83H,  $\text{C}_3\text{H}_2$  (**3a**)), 1.34–1.49 (m, 0.17H,  $\text{C}_3\text{H}_2$  (**3b**)), 1.62–1.73 (m, 0.83H,  $\text{C}_3\text{H}_2$  (**3a**)), 1.79–1.91 (m, 1H,  $\text{C}_4\text{H}_2$ ), 1.98–2.13 (m, 1.83H,  $\text{C}_4\text{H}_2$  and  $\text{C}_1\text{H}_2$  (**3a**)), 2.27–2.37 (m, 0.17H,  $\text{C}_1\text{H}_2$  (**3b**)), 2.47–2.59 (m, 1H,  $\text{C}_2\text{H}$ ), 2.69–2.85 (m, 1H,  $\text{C}_1\text{H}_2$ ), 7.10–7.47 (m, 28H, phenyl-H), 7.76–7.84 (m, 2H, phenyl-H).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 18.00 (s, 0.83P (**3a**)), = 17.58 (s, 0.17P (**3b**)), 66.8 (br, 1P), 87.0 (br, 1P).

#### 4.4.1. Separation of the diastereomers

To a  $\text{CH}_2\text{Cl}_2$  solution pentane was slowly added, then the solution was cooled to  $-18^\circ\text{C}$ . Red crystals, suitable for X-ray analysis, of pure **3a** were obtained, m.p. 198–201°C.  $[\alpha]_D^{25} = -125$  (c 1.17,  $\text{CH}_2\text{Cl}_2$ ).

#### 4.5. $\text{Co}(\text{CO})(\text{NO})(1,2,5\text{-triphos})$ **4a,4b**

A solution of  $\text{Co}(\text{CO})_3(\text{NO})$  (0.16 g, 0.93 mmol) and (R)-(+)-1,2,5-tris(diphenylphosphanyl)pentane(1,2,5-triphos) [25] (0.70 g, 1.12 mmol) in 125 ml of THF was refluxed for 22 h. Chromatography on silica with THF:petroleum ether 40–60 (3:5) afforded an orange band. After removal of the solvent **4a,4b** was obtained as an orange solid. Yield 0.68 g (99%), molar ratio **4a:4b** 63:37, m.p. 115°C.  $[\alpha]_D^{25} = -68$  (c 0.93,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.63–0.75 (m, 0.37H,  $\text{C}_4\text{H}_2$  (**4b**)), 1.01–1.12 (m, 0.63H,  $\text{C}_4\text{H}_2$  (**4a**)), 1.14–1.26 (m, 1H,  $\text{C}_3\text{H}_2$ ), 1.29–1.71 (m, 4H,  $\text{C}_3\text{H}_2$ ,  $\text{C}_4\text{H}_2$  and  $\text{C}_5\text{H}_2$ ), 1.93–2.41 (m, 2.63H,  $\text{C}_1\text{H}_2$  and  $\text{C}_2\text{H}$  (**4a**)), 2.56–2.72 (m, 0.37H,  $\text{C}_2\text{H}$  (**4b**)), 6.87–7.56 (m,

26H, phenyl-H), 7.65–7.98 (m, 4H, phenyl-H).  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  -15.63 (s, 0.37P (**4b**)), -15.57 (s, 0.63P (**4a**)), 68.6 (br, 1P), 87.2 (br, 1P).

#### 4.6. $\text{Co}(\text{CO})(\text{NO})(\text{PN1})$ **5a,5b**

A solution of  $\text{Co}(\text{CO})_3(\text{NO})$  (0.95 g, 5.5 mmol) and (R)-(+)-(diphenyl)-2-[N-1'-phenylethylaldimino]phenylphosphane (PN1) [26] (2.0 g, 5.1 mmol) in 60 ml of toluene was stirred for 12 h at  $80^\circ\text{C}$ . After removal of the solvent the black residue was chromatographed on silica. Elution with toluene:petroleum ether 40–60 (1:1) gave a brown band which provided **5a,5b** after evaporating the solvent. Recrystallization from ethanol yielded black crystals with a molar ratio of **5a:5b** 50:50. Yield 1.9 g (73%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.87 (d,  $^3J(\text{CH}_3\text{-CH}) = 6.7$  Hz, 3H,  $\text{CH}_3$ ), 1.93 (d,  $^3J(\text{CH}_3\text{-CH}) = 6.7$  Hz, 3H,  $\text{CH}_3$ ), 5.16 (q,  $^3J(\text{CH}_3\text{-CH}) = 6.7$  Hz, 1H, CH), 5.26 (q,  $^3J(\text{CH}_3\text{-CH}) = 6.7$  Hz, 1H, CH), 7.14–7.54 (m, 38H, phenyl-H) 8.36 (d,  $^4J(\text{CH-P}) = 1.6$  Hz, 1H, =CH), 8.43 (d,  $^4J(\text{CH-P}) = 1.6$  Hz, 1H, =CH).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  53.3 (br).

#### 4.7. $\text{Co}(\text{CO})(\text{NO})(\text{PN2})$ **6a,6b**

The mixture of  $\text{Co}(\text{CO})_3(\text{NO})$  (1.0 g, 5.8 mmol) and (R)-(-)-(diphenyl)-2-[N-1'-hydroxybut-2'-ylaldimino]phenylphosphane (PN2) [27] (1.8 g, 5.0 mmol) in 50 ml of toluene was stirred for 16 h at  $80^\circ\text{C}$ . The solvent was evaporated and the residue was chromatographed on silica. Elution with ethyl acetate:petroleum ether 40–60 (2:1) gave a brown band. After removal of the solvent and recrystallization from ethanol black crystals were obtained. The molar ratio of **6a:6b** was 50:50. Yield 1.58 g (69%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.49 (t,  $^3J(\text{CH}_3\text{-CH}_2) = 7.4$  Hz, 3H,  $\text{CH}_3$ ), 0.81 (t,  $^3J(\text{CH}_3\text{-CH}_2) = 7.4$  Hz, 3H,  $\text{CH}_3$ ), 1.43–2.25 (m, 6H, C=CH<sub>2</sub> and OH), 3.28–3.69 (m, 4H, O=CH<sub>2</sub>), 4.21–4.31 (m, 1H, CH), 4.42–4.48 (m, 1H, CH), 7.03–7.59 (m, 28H, phenyl-H), 8.29 (s, 2H, =CH).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  53.0 (br).

#### 4.8. $\text{Co}(\text{CO})(\text{NO})(\text{NN1})$ **7a,7b**

Under an atmosphere of argon a solution of  $\text{Co}(\text{CO})_3(\text{NO})$  (1.6 g, 9.3 mmol) and (S)-(-)- $\alpha$ -methyl-N-(2-pyridinylmethylene)benzenemethanamine (NN1) [28,29] (1.8 g, 8.6 mmol) in 50 ml of toluene was stirred for 4 h at  $50^\circ\text{C}$ . Then the solution was filtered and concentrated. After addition of petroleum ether 40–60 the solution was cooled to  $-18^\circ\text{C}$  to afford black crystals of **7a,7b**, molar ratio 50:50. Yield 1.9 g (73%).  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ ):  $\delta$  1.76 (d,  $^3J(\text{CH}_3\text{-CH}) = 6.6$  Hz, 3H,  $\text{CH}_3$ ), 1.83 (d,  $^3J(\text{CH}_3\text{-CH}) = 6.6$  Hz, 3H,  $\text{CH}_3$ ), 5.17 (m, 2H, CH), 7.08–7.75 (m, 18H, phenyl-H)



and py-H), 8.84 (d,  $^1J(\text{CH}-\text{CH}) = 3.0\text{ Hz}$ , 1H, =CH), 8.90 (d,  $^1J(\text{CH}-\text{CH}) = 3.0\text{ Hz}$ , 1H, =CH).

#### 4.9. *Co(CO)(NO)(NN2) 8a,8b*

$\text{Co}(\text{CO})_3(\text{NO})$  (1.6 g, 9.3 mmol) and (S)-(-)- $\alpha$ -methyl-*N*-[1-(2-pyridinyl)ethylidene]benzenemethanamine (NN2) [29] (2.0 g, 8.9 mmol) were treated the same way as described for **7a,7b**. The complex **8a,8b** was obtained as black crystals. Yield 2.3 g (75%).  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ):  $\delta$  1.87 (d,  $^3J(\text{CH}_3-\text{CH}) = 6.5\text{ Hz}$ , 3H,  $\text{CH}_3$ ), 1.92 (d,  $^3J(\text{CH}_3-\text{CH}) = 6.5\text{ Hz}$ , 3H,  $\text{CH}_3$ ), 2.53 (s, 6H<sub>1</sub>, =C- $\text{CH}_3$ ), 5.47 (q,  $^3J(\text{CH}_3-\text{CH}) = 6.5\text{ Hz}$ , 1H, CH), 5.55 (q,  $^3J(\text{CH}_3-\text{CH}) = 6.5\text{ Hz}$ , 1H, CH), 7.19–8.20 (m, 16H, phenyl-H and py-H3, H4, H5), 9.36 (m, 2H, py-H6).

#### 4.10. X-ray structure analysis of **1a**

X-ray diffraction data were collected at 20°C with a Syntex-Nicolet R3 diffractometer using Mo K $\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ) with a graphite crystal monochromator. The structure was solved using Patterson–Fourier methods with SHELXLS Release 4.2/800 programs [30] on a Micro VAX II computer. The hydrogen atoms were calculated by the option HFIX of the SHELXLS program package.

#### 4.11. X-ray structure analysis of **3a**

X-ray diffraction data were collected at –70°C with a Siemens Stoe AED II diffractometer using Mo K $\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ) with a graphite crystal monochromator. The structure was solved using direct methods with SHELXTL PLUS Release 4.2/800 programs [30] on a Micro VAX II computer. The hydrogen atoms were calculated by the option HFIX of the SHELXTL PLUS program package.

#### Acknowledgements

We thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the BASF AG, Ludwigshafen, Germany, for support of this work.

#### References

- [1] H. Brunner, J. Bügler, B. Nuber, *Tetrahedron Asymm.* 7 (1996) 3095.
- [2] H. Brunner, *Angew. Chem.* 81 (1969) 395; *Angew. Chem., Int. Ed. Engl.* 8 (1969) 382.
- [3] H. Brunner, *Adv. Organomet. Chem.* 18 (1980) 151.
- [4] G. Consiglio, F. Morandini, *Chem. Rev.* 87 (1987) 761.
- [5] K. Blackburn, S.G. Davies, M. Whittaker, in I. Bernal (Ed.), *Chemical Bonds – Better Ways to Make Them and to Break Them*, Elsevier, New York, 1989, p. 141.
- [6] G.A. Stark, M.A. Dewey, G.B. Richter-Addo, D.A. Knight, A.M. Arif, J.A. Gladysz, in H. Werner, J. Sundermeyer (Eds.), *Stereoselective Reactions of Metal-Activated Molecules*, Vieweg, Stuttgart, 1995, p. 51.
- [7] H. Brunner, W. Miehl, *Angew. Chem.* 95 (1983) 162; *Angew. Chem., Int. Ed. Engl.* 22 (1983) 84.
- [8] W. Hieber, J. Ellermann, *Chem. Ber.* 96 (1963) 1643.
- [9] H. Brunner, H.-D. Schindler, E. Schmidt, M. Vogel, *J. Organomet. Chem.* 24 (1974) 515.
- [10] A.W. Coleman, P.B. Hitchcock, M.F. Lappert, R.K. Maskell, J.H. Müller, *J. Organomet. Chem.* 296 (1985) 173.
- [11] A.W. Coleman, P.B. Hitchcock, M.F. Lappert, R.K. Maskell, J.H. Müller, *J. Organomet. Chem.* 250 (1983) C9.
- [12] M.F. Lappert, P.L. Pye, *J. Chem. Soc., Dalton Trans.* (1977) 2172.
- [13] E.M. Thornsteinson, F. Basolo, *Inorg. Chem.* 5 (1966) 1691.
- [14] W.D. Horrocks, R.C. Taylor, *Inorg. Chem.* 2 (1963) 723.
- [15] J.T. Lin, S.Y. Wang, Y.C. Chou, M.L. Gong, Y.-M. Shiows, H.-M. Gau, Y.S. Wen, *J. Organomet. Chem.* 508 (1996) 183.
- [16] E.P. Ross, G.R. Dobson, *Inorg. Chem.* 6 (1967) 1256.
- [17] D. Rogers, *Acta Crystallogr.* A37 (1981) 734.
- [18] V.G. Albano, P.L. Bellon, G. Ciani, *J. Organomet. Chem.* 38 (1972) 155.
- [19] D. Carmona, F.J. Lahoz, L.A. Oro, M.P. Lamata, F. Viguri, E.S. Jose, *Organometallics* 15 (1996) 2961.
- [20] H. Brunner, A. Winter, J. Breu, *J. Organomet. Chem.*, in press.
- [21] W. Hieber, E.O. Fischer, E. Bückly, *Z. Anorg. Allg. Chem.* 269 (1952) 308.
- [22] M.D. Fryzuk, B. Bosnich, *J. Am. Chem. Soc.* 100 (1978) 5491.
- [23] H. Brunner, W. Pieronczyk, *Angew. Chem.* 91 (1979) 655; *Angew. Chem., Int. Ed. Engl.* 18 (1979) 620.
- [24] H. Brunner, W. Pieronczyk, B. Schönhammer, K. Streng, I. Bernal, *J. Korp.* *Chem. Ber.* 114 (1981) 1137.
- [25] H. Brunner, H.-J. Lautenschlager, *Synthesis* (1989) 706.
- [26] H. Brunner, A.F.M.M. Rahman, *Chem. Ber.* 117 (1984) 710.
- [27] H. Brunner, J. Fürst, *Inorg. Chim. Acta* 220 (1994) 63.
- [28] F. Nerdel, K. Becker, G. Kresze, *Chem. Ber.* 89 (1956) 2862.
- [29] H. Brunner, B. Reiter, G. Riepl, *Chem. Ber.* 117 (1984) 1330.
- [30] G.M. Sheldrick, SHELXLS, SHELXTL PLUS, A Program for Crystal Structure Determination, Siemens Analytical X-Ray Instruments, Madison, WI, 1990.