ELSEVIER

Journal of Organometallic Chemistry 579 (1999) 1–4

Journal of Organo metallic Chemistry

# Complete carbonyl substitution in tricarbonylnitrosylcobalt[1]

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

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

Received 25 February 1997

---

**Abstract**

In addition to the main product Co(CO)(NO)($PR_3$)[(*S*)-CNCH(Me)(Ph)], chiral at the cobalt atom, the reaction of Co(CO)(NO)$(PR_3)_2$ with the isocyanide (*S*)-(−)-CNCH(Me)(Ph) yields two complexes as by-products in which the carbonyl group has been substituted. The new complexes Co(NO)$(PR_3)_2$[(*S*)-CNCH(Me)(Ph)] **1**, **3** and Co(NO)($PR_3$)[(*S*)-CNCH(Me)(Ph)]$_2$ **2**, **4** were characterized by IR, NMR and FD mass spectra. R can be phenyl (**1**, **2**) or *p*-tolyl (**3**, **4**). The reaction of Co(CO)(NO)[(*R*)-prophos] with the isocyanide CN$^t$Bu also results in a substitution of the carbonyl group. The crystal structure of Co(NO)(CN$^t$Bu)[(*R*)-prophos] **5** was determined by X-ray analysis. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Cobalt complex; Carbonyl substitution; X-ray structure analysis

---

## 1. Introduction

Tricarbonylnitrosylcobalt and its mono and disubstituted derivates have been extensively studied over the last 40 years. In most of the studies aimed at the replacement of carbonyl groups by other ligands it has been stated that the third carbonyl group of $Co(CO)_3(NO)$ resists substitution [1,2]. This is due in part to the well-known electron-withdrawing effect of the carbonyl group compared to other ligands. Moreover, as substitution takes place primarily by an associative mechanism, the steric effect seems to be the main reason for the reluctance of the third carbonyl group to substitution. The transition state has trigonal-bipyramidal geometry, which is difficult to achieve when two bulky ligands are already present [3–6]. Therefore, all known complexes of the type $Co(NO)L_3$ in which L is a ligand different from CO have been prepared by other methods [7–10]. In the course of our investigation of chiral carbonylnitrosylcobalt complexes [11,12] we have found that the substitution of the third carbonyl group can occur.

## 2. Synthesis

We intended to synthesize complexes of the type Co(CO)(NO)($PR_3$)(CNR*) with R = phenyl or *p*-tolyl and CNR* = (*S*)-(−)-CNCH(Me)(Ph). For that purpose a mixture of Co(CO)(NO)$(PR_3)_2$ with a small excess of free CNR* in toluene was heated to 90°C for 4 h. After work-up by chromatography the desired complex was obtained as the main product. However, there were two by-products which were identified by IR, NMR and FD mass spectra to be Co(NO)$(PR_3)_2$(CNR*) **1**, **3** and Co(NO)($PR_3$)$(CNR^*)_2$ **2**, **4**, respectively (Scheme 1).

We repeated the reaction with a complex containing the bidentate ligand (*R*)-prophos instead of two monodentate ligands. In 19% yield the carbonyl exchange product **5** was formed (Scheme 2).

The IR spectra of all the new complexes **1**–**5** exhibit only one nitrosyl band in the range of 1650–1665

---

[1] Dedicated to Professor Dr C.G. Kreiter on the occasion of his 60th birthday.

* Corresponding author. Tel.: +49-9419434441; fax: +49-9-419434439.

PII: S0022-328X(97)00194-0

cm$^{-1}$. This is in accord with the values found for the complexes of the type Co(NO)$L_3$ [7–9]. There is no band in the region 1900–2000 cm$^{-1}$ of the carbonyl frequencies [13]. Complexes **1**, **3** and **5** show one further band between 2060 and 2100 cm$^{-1}$, whereas complexes **2** and **4** exhibit two bands between 2070 and 2130 cm$^{-1}$. These bands are attributed to the CNR ligands.

## 3. X-ray structure analysis of 5

A single crystal of **5** for X-ray structure analysis was obtained from a sample recrystallized from benzene-$d_6$/ether. The crystal contains one disordered molecule of benzene-$d_6$ per unit cell. In Table 1 crystal data and data of the structure refinement are summarized and in Table 2 selected bond distances and angles are given. The molecular structure of **5** and the atom numbering scheme is shown in Fig. 1.

The complex **5** is formed as a pair of diastereomers which differ only in the configuration at the cobalt center. By refinement of the least-squares variable $\eta$ we could determine the absolute configuration [14] ($\eta = 1.02(6)$). We found an $S_{Co},R_C$-configuration. However, further assignments are not possible, as the measured crystal was taken from a 65:35 mixture of diastereomers (see Section 4).

The coordination around the cobalt atom is distorted tetrahedral. The Co–P distances (2.187 Å and 2.192 Å) as well as the Co–N distance (1.632 Å) are near to the values found for the parent compound Co(CO)(NO)[(*R*)-prophos] [11]. The same holds for all the angles around the cobalt center (see Table 2). The NO group is found to be nearly linear (angle Co–N–O 178.5°) as well as the Co–C–N–C group (angles Co–C–N 177.0° and C–N–C 177.8°). Different from Co(CO)(NO)[(*R*)-prophos], the methyl group of the prophos ligand is in the more common equatorial position of the five-membered chelate ring [11,15].

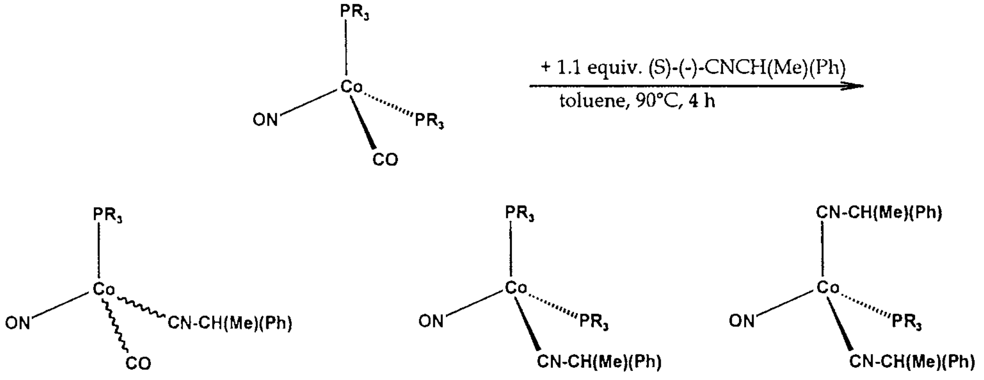
## 4. Experimental

All reactions were carried out under an atmosphere of dried nitrogen using standard Schlenk techniques. Infrared spectra were obtained on a Perkin–Elmer Paragon 1000 PC FT-IR. $^1$H- and $^{31}$P-NMR were recorded on a Bruker ARX 400 spectrometer [400.13 MHz ($^1$H) and 161.98 MHz ($^{31}$P), solvent benzene-$d_6$]. FD mass spectra were determined on a Finnigan MAT 95 instrument. Elemental analyses were carried out by the microanalytical laboratory of the University of Regensburg.

The complexes Co(CO)(NO)(PPh$_3$)$_2$, Co(CO)(NO)-[P(*p*-tolyl)$_3$]$_2$ and Co(CO)(NO)(prophos) as well as the isocyanides (*S*)-(−)-CNCH(Me)(Ph) and CN–$^t$Bu were prepared according to literature methods [2,16,17].

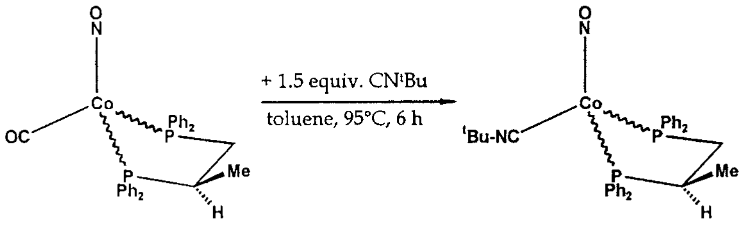
### 4.1. Synthesis of Co(NO)(PPh$_3$)$_2$((S)-CNCH(Me)(Ph)] 1 and Co(NO)(PPh$_3$)[(S)-CNCH(Me)(Ph)]$_2$ 2

A mixture of Co(CO)(NO)(PPh$_3$)$_2$ (2.00 g, 3.12 mmol) and (*S*)-(−)-CNCH(Me)(Ph) (0.43 g, 3.28 mmol) in 40 ml of toluene was stirred for 4 h at 90°C. After removal of the solvent the brown residue was chromatographed on silica. With toluene/petroleum ether 40–60 2:1 (by volume) a first red band was eluted which provided Co(CO)(NO)(PPh$_3$)[(*S*)-CNCH(Me)-(Ph)] after evaporating the solvent. Further elution with toluene/petroleum ether 40–60 10:1 afforded a brown band of **1** and with toluene/acetone



| | | |
|---|---|---|
| R = phenyl: Co(CO)(NO)(PPh$_3$)(CNR*) | 1 Co(NO)(PPh$_3$)$_2$(CNR*) | 2 Co(NO)(PPh$_3$)(CNR*)$_2$ |
| 65% | 11% | 19% |
| R = p-tolyl: Co(CO)(NO)[P(p-tolyl)$_3$](CNR*) | 3 Co(NO)[P(p-tolyl)$_3$]$_2$(CNR*) | 4 Co(NO)[P(p-tolyl)$_3$](CNR*)$_2$ |
| 51% | 6% | 14% |

Scheme 1.



**5** Co(NO)(CN<sup>t</sup>Bu)[(R)-prophos] 19%

Scheme 2.

15:1 a dark red band of **2** was obtained. The complexes **1** and **2** were recrystallized from toluene/ether.

**1**: Yield 250 mg (11%) brown crystals, m.p. 159°C (dec.). Anal. found (%): C, 72.55; H, 5.32; N, 3.77. $C_{45}H_{39}CoN_2OP_2$ Calc.: C, 72.58; H, 5.28; N, 3.76. FD MS (toluene): $m/z = 744.1$. IR (KBr, $cm^{-1}$): 2073 vs ($\nu_{CN}$); 1665 vs ($\nu_{NO}$). $^1$H-NMR: $\delta$ (ppm, $J$ (Hz)) 1.00 (d, $^3J_{HH}$ 6.8, 3H, $CH_3$); 4.17 (tq, $^3J_{HH}$ 6.8, $^5J_{PH}$ 2.5, 1H, CH); 6.79–7.05 (m, 23H, phenyl-H), 7.51–7.58 (m, 12H, phenyl-H). $^{31}$P-NMR: $\sigma$ (ppm) 62.8 (br).

**2**: Yield 370 mg (19%) dark red crystals, m.p. 127–130°C. Anal. found (%): C, 69.51; H, 5.46; N, 6.79. $C_{36}H_{33}CoN_3OP$ Calc.: C, 70.47; H, 5.42; N, 6.85. FD MS (toluene): $m/z = 613.2$. IR (KBr, $cm^{-1}$): 2115 vs, 2072 vs ($\nu_{CN}$); 1651 vs ($\nu_{NO}$). $^1$H-NMR: $\delta$ (ppm, $J$ (Hz)) 1.03, 1.06 (d, $^3J_{HH}$ 6.8, 6H, $CH_3$); 4.19–4.27 (m, 2H, CH); 6.84–7.08 (m, 19H, phenyl-H), 7.79–7.83 (m, 6H, phenyl-H). $^{31}$P-NMR: $\delta$ (ppm) 65.3 (br).

### *4.2. Synthesis of Co(NO)[P(p-tolyl)$_3$]$_2$[(S)-CNCH(Me)(Ph)] **3** and Co(NO)[P(p-tolyl)$_3$][(S)-CNCH(Me)(Ph)]$_2$ **4***

A mixture of 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) was treated as described above.

**3**: Yield 71 mg (6%) brown crystals, m.p. 101°C (dec.). Anal. found (%): C, 73.08; H, 6.09; N, 3.49. $C_{51}H_{51}CoN_2OP_2$ Calc.: C, 73.90; H, 6.20; N, 3.38. FD MS (toluene): $m/z = 828.2$. IR (KBr, $cm^{-1}$): 2060 vs ($\nu_{CN}$); 1664 vs ($\nu_{NO}$). $^1$H-NMR: $\delta$ (ppm, $J$ (Hz)) 1.12 (d, $^3J_{HH}$ 6.6, 3H, $CH_3$); 2.02 (s, 18H, aryl-$CH_3$); 4.28 (tq, $^3J_{HH}$ 6.6, $^5J_{PH}$ 2.5, 1H, CH); 6.84–7.01 (m, 17H, phenyl-H), 7.58–7.64 (m, 12H, phenyl-H). $^{31}$P-NMR: $\delta$ (ppm) 60.3 (br).

**4**: Yield 140 mg (14%) dark red crystals, m.p. 90°C (dec.). Anal. found (%): C, 71.01; H, 5.79; N, 6.60. $C_{39}H_{39}CoN_3OP$ Calc.: C, 71.44; H, 6.00; N, 6.41. FD MS (toluene): $m/z = 655.1$. IR (KBr, $cm^{-1}$): 2110 sh, 2061 vs ($\nu_{CN}$); 1670 vs ($\nu_{NO}$). $^1$H-NMR: $\delta$ (ppm, $J$ (Hz)) 1.07, 1.10 (d, $^3J_{HH}$ 6.8, 6H, $CH_3$); 1.95 (s, 9H, aryl-$CH_3$); 4.52–4.62 (m, 2H, CH); 6.80–7.05 (m, 16H, phenyl-H), 7.72–7.78 (m, 6H, phenyl-H). $^{31}$P-NMR: $\delta$ (ppm) 63.0 (br).

### *4.3. Synthesis of Co(NO)(CN$^t$Bu)[(R)-prophos] **5***

A solution of Co(CO)(NO)[(*R*)-prophos] (1.00 g, 1.89 mmol) and CN$^t$Bu (0.23 g, 2.77 mmol) in 25 ml of toluene was stirred for 6 h at 95°C. The solvent was evaporated and the residue chromatographed on silica. Elution with toluene afforded two red bands. The first band contained the starting material Co(CO)(NO)[(*R*)-prophos] (51%). From the second band complex **5** was obtained after removal of the solvent Recrystallization from benzene/ether gave red crystals. The molar ratio of the two diastereomers **5a**:**5b**, which differ only in the cobalt configuration, was 65:35. Yield **5**: 210 mg (19%), m.p. 155°C (dec.). Anal. found (%): C, 68.22; H, 6.45; N, 4.29. $C_{32}H_{35}CoN_2OP_2 \cdot C_6H_6$ Calc.: C, 68.88; H, 6.24; N, 4.23. FD MS (toluene): $m/z = 584.1$. IR (KBr, $cm^{-1}$): 2099 vs ($\nu_{CN}$); 1655 vs ($\nu_{NO}$). $^1$H-NMR: $\delta$ (ppm, $J$ (Hz)) 0.60–0.65 (m, 5.85H (**5a**), $C(CH_3)_3$ and 1.05H (**5b**), $CH_3$); 0.78 (s, 3.15H (**5b**), $C(CH_3)_3$); 0.82 (dd, $^3J_{HH}$ 6.9, $^3J_{PH}$ 11.2, 1.95H (**5a**), $CH_3$); 2.00–2.36 (m, 2H, $CH_2$ and 0.65H (**5a**), CH)*; 2.64–2.72 (m, 0.35H (**5b**), CH), 6.92–7.21 (m, 12H, phenyl-H); 7.41–8.15 (m, 8H, phenyl-H). *$^1$H-{$^{31}$P}: 2.02–2.13 (m, 1.35H, $CH_2$);

Table 1
Summary of crystal data and structure refinement for **5**

| | |
|---|---|
| *Crystal parameters* | |
| Formula | $C_{32}H_{35}CoN_2OP_2 \cdot C_6D_6$ |
| Mol wt | 668.68 |
| Color and shape | Red, parallel-epipedic |
| Size (mm) | $0.20 \times 0.25 \times 0.35$ |
| Crystal system; space group | Triclinic; P1 (1) |
| $a$; $b$; $c$ (Å) | 9.857(2); 9.978(2); 11.029(2) |
| $\alpha$; $\beta$; $\gamma$ (deg) | 73.92(1); 67.73(1); 64.25(1) |
| $V$ (Å$^3$); $Z$ | 895.9(3); 1 |
| $D_{calc}$ (g $cm^{-1}$) | 1.23 |
| $F$(000) | 348 |
| $\mu$ ($mm^{-1}$) | 0.60 |
| *Data refinement* | |
| No. of LS parameters | 366 |
| Largest shift/e.s.d. in final cycle | 0.014 |
| $\Delta\rho_{min}$; $\Delta\rho_{max}$ (e Å$^{-3}$) | −0.55; 1.00 |
| $R^a$; $R_w^b$ | 0.063; 0.053 |

$^a R = \Sigma\|F_o - F_c\|/|F_c|$.

$^b R_w = \Sigma\|F_o| - |F_c\|w^{1/2}/|F_c|w^{1/2}, w = 1/\sigma^2(F_o)$.

Table 2
Selected bond lengths (Å) and angles (deg) of **5** with estimated standard deviations in parentheses

| | | | |
|---|---|---|---|
| Co–P1 | 2.187(3) | P1–C1 | 1.863(8) |
| Co–P2 | 2.192(2) | P1–C7 | 1.822(13) |
| Co–N2 | 1.632(8) | P1–C31 | 1.842(7) |
| Co–C25 | 1.833(9) | P2–C13 | 1.830(7) |
| N2–O1 | 1.213(10) | P2–C19 | 1.816(13) |
| C25–N1 | 1.176(13) | P2–C30 | 1.881(8) |
| N1–C26 | 1.435(13) | C30–C31 | 1.534(16) |
| P1–Co–P2 | 88.3(1) | Co–C25–N1 | 177.0(7) |
| P1–Co–N2 | 121.9(4) | C25–N1–C26 | 177.8(11) |
| P2–Co–N2 | 120.4(3) | Co–P1–C31 | 107.1(3) |
| P1–Co–C25 | 102.8(3) | Co–P2–C30 | 107.5(3) |
| P2–Co–C25 | 99.4(3) | P1–C31–C30 | 110.3(6) |
| N2–Co–C25 | 118.2(4) | C31–C30–P2 | 104.9(5) |
| Co–N2–O1 | 178.5(10) | P2–C30–C32 | 117.4(7) |

2.23 (dd, $^2J_{HH}$ 13.9, $^3J_{HH(cis)}$ 5.2, 0.65H (**5a**), $CH_2$); 2.31–2.35 (m, 0.65H (**5a**), CH). $^{31}$P-NMR: $\delta$ (ppm) 74.2 (br, 1P); 94.1 (br, 1P).

### 4.4. X-ray structure analysis of **5**

X-ray diffraction data were collected at 20°C with a Syntex–Nicolet R3 diffractometer using Mo–$K_\alpha$ radiation ($\lambda = 0.71073$ Å) with a graphite-crystal monochromator. Data were collected by a $\omega$-scan in the range $2\Theta = 3.0°–52.5°$ (*hkl* ranges: 0–13; −13–13; −14–14). A total no. of 5400 unique reflections was observed, of which 4202 had $I > 2.5\sigma_I$. The determination of the lattice constants was done with 32 reflections ($2\Theta = 9.0°–24.0°$) and the empirical absorption correction with 6 reflections ($2\Theta = 8.0°–33.0°$). For the determination of the absolute configuration Friedel pairs have been measured in the range $2\Theta = 3.0°–42.0°$ (*h*: −10–(−1); *k*: −11–11; *l*: −12–12). Min. and max. transmissions factors were 0.94 and 1.00. The structure was solved using direct methods with SHELXTL PLUS Release 4.2/800 [18] on a PC. The hydrogen atoms were calculated by the option HFIX of the SHELXTL PLUS program package. Further details of the structure determination have been deposited with the number CSD 406561 at the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen.

## Acknowledgements

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

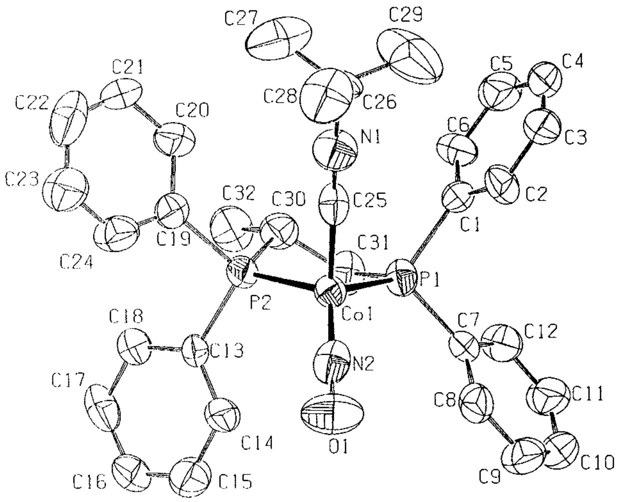


Fig. 1. Molecular structure of **5** and the atom numbering scheme [19].

## References

[1] L. Malatesta, A. Araneo, J. Chem. Soc. (1957) 3803.
[2] T.A. Manuel, Adv. Organomet. Chem. 3 (1965) 181.
[3] E.M. Thorsteinson, F. Basolo, J. Am. Chem. Soc. 88 (1966) 3929.
[4] E.M. Thorsteinson, F. Basolo, Inorg. Chem. 5 (1966) 1691.
[5] G. Cardaci, A. Foffani, G. Distefano, G. Innorta, Inorg. Chim. Acta 1 (1967) 340.
[6] S. Zhang, G.R. Dobson, Inorg. Chem. 28 (1989) 324.
[7] L. Malatesta, A. Sacco, Z. Anorg. Allg. Chem. 274 (1953) 341.
[8] W. Hieber, K. Heinicke, Z. Anorg. Allg. Chem. 316 (1962) 305.
[9] S. Bhaduri, K. Grundy, B.F.G. Johnson, J. Chem. Soc., Dalton Trans. (1977) 2085.
[10] W.E. Carrol, M. Green, A.M.R. Galas, M. Murray, T.W. Turney, A.J. Welch, P. Woodward, J. Chem. Soc., Dalton Trans. (1980) 80.
[11] H. Brunner, P. Faustmann, A. Dietl, B. Nuber, J. Organomet. Chem. 542 (1997) 255.
[12] H. Brunner, P. Faustmann, J. Organomet. Chem. 556 (1998) 129.
[13] W.D. Horrocks, R.C. Taylor, Inorg. Chem. 2 (1963) 723.
[14] D. Rogers, Acta Crystallogr. A37 (1981) 734.
[15] H. Brunner, A. Winter, J. Breu, J. Organomet. Chem. 553 (1998) 285.
[16] W. Hieber, J. Ellermann, Chem. Ber. 96 (1963) 1643.
[17] R. Appel, R. Kleinstück, K.-D. Ziehn, Angew. Chem. 83 (1971) 143; Angew. Chem. Int. Ed. Engl. 10 (1971) 132.
[18] G.M. Sheldrick, SHELXTL PLUS Release 4.2/800, A Program for Crystal Structure Determination, Siemens Analytical X-Ray Instruments, Madison, WI, 1990.
[19] PLATON, A.L. Spek, Acta Crystallogr. A46 (1990) C34.