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The first alkyne-dicobaltcarbonyl complex with a bidentate chiral ligand with Co–P and Co–N coordination

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Abstract

Treatment of the phenylacetylene dicobalthexacarbonyl complex with (*R*)-2-(2-diphenylphosphinophenyl)-4-phenyl-4,5-dihydrooxazole produces a 85:15 mixture of the diastereomer complexes **2** and **3** that can be separated by recrystallization; the X-ray structure of **2** shows that one cobalt atom is coordinated to both the phosphorus and nitrogen atoms of the ligand. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The stable, easily obtained complexes of $Co_2(CO)_8$ with alkynes (Fig. 1), first described by Greenfield and co-workers more than 40 years ago [1], nowadays enjoy widespread use in synthetic chemistry [2], both in the protection of triple bonds [3] and as reagents in a variety of carbon–carbon and carbon–heteroatom bond formation processes [4]. Moreover, the replacement of one or more CO groups by ligand substitution of the parent hexacarbonyl species gives rise to a wide range of new complexes. While the vast majority of these substituted complexes involve the use of mono- [5] and bidentate [6] phosphine or phosphite ligands (usually coordinating a Ψ-axial position), there are some examples of sulfur [7] and nitrogen [8] containing alkyne pentacarbonyldicobalt complexes. Much more scarce are the examples in which the cobalt atoms are simultaneously coordinated to two different heteroatoms. Only very recently, Mays and co-workers [9] have described the synthesis and characterization of complexes of the general structure $[Co_2(\mu\text{-}R^1CCR^2)(\mu\text{-}PPh_2CH_2SR^3)(CO)_4]$, in which the bidentate ligand bridges the two cobalt atoms. On the other hand, alkyne-dicobaltcarbonyl complexes substituted by bidentate phosphorus-nitrogen ligands are not known.

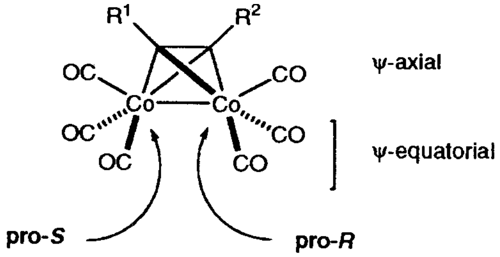

Fig. 1. General structure of an alkyne-dicobalthexacarbonyl complex. It is assumed that R^1 has higher priority than R^2 according to the sequence rule.

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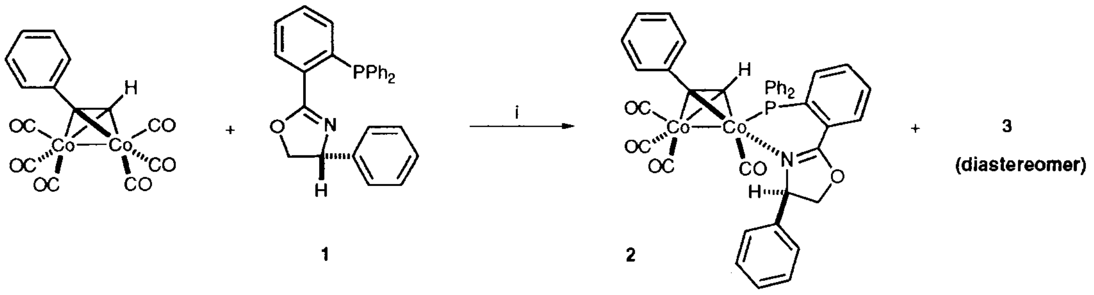


Scheme 1. Reagents and conditions: (i) toluene, 60°C, 2 h, 76%. **2**:**3** (85:15) [70% de].

When $R^1 \neq R^2$ and both are non chiral groups, the two cobalt atoms in the alkyne-dicobaltcarbonyl complex are enantiotopic (Fig. 1). Depending on whether the coordination takes place with the pro-*R* or the pro-*S* cobalt, the reaction with a chiral monodentate ligand can lead to two diastereomers. Alkyne-dicobaltpentacarbonyl complexes with chiral phosphine ligands [10,11] were first prepared owing to their interest in the development of enantioselective Pauson–Khand reactions [12]. Pauson and Brunner [10a], by heating the phenylacetylene dicobalt hexacarbonyl complex with (*R*)-(+)-glyphos obtained two diastereomeric complexes in a 3:2 ratio (20% diastereomeric excess); after separation, both diastereomeric complexes (whose absolute configuration was not determined) reacted with norbornadiene at 40°C to give the expected Pauson–Khand adduct with excellent ee, albeit in low yields. At higher temperatures, interconversion between both complexes was very fast. Later on, Kerr et al. [10b] found that the use of anhydrous *N*-methylmorpholine-*N*-oxide under mild conditions prevented the equilibration of the complexes and allowed the use of alkynes different from phenylacetylene. Nevertheless, no chiral phosphines other than (*R*)-(+)-glyphos were investigated, and the diastereomer complexes had to be separated by preparative HPLC.

2-(2-Phosphinoaryl)dihydrooxazoles constitute a recently introduced class of chiral bidentate ligands, that have been successfully employed in enantioselective catalytic allylic substitution reactions and in other metal-mediated asymmetric transformations [13]. The high enantioselectivity observed in these processes is due to the formation of catalytically active complexes in which the metal coordinates both to the phosphorus and the nitrogen atoms of the ligand.

Having these precedents in mind, we decided to investigate the use of chiral 2-(2-phosphinoaryl)-dihydrooxazoles as bidentate ligands of alkyne-dicobaltcarbonyl complexes. In this work we disclose our initial studies on this field, which have led to the synthesis and characterization of the first alkyne-dicobaltcarbonyl complex coordinated with a chiral 2-(2-phosphinoaryl)dihydrooxazole.

2. Results and discussion

The ligand (−)-(*R*)-2-(2-diphenylphosphinophenyl)-4-phenyl-4,5-dihydrooxazole (**1**) was easily prepared from (*R*)-(−)-2-phenylglycinol by the procedure described by Helmchen et al. [14], and was reacted in toluene solution at 60°C during 2 h with the phenylacetylene dicobalthexacarbonyl complex, to give after chromatographic purification a 85:15 mixture (70% de) of complexes **2** and **3** in 76% yield (Scheme 1). Fractional recrystallization of this mixture from hexane methylene chloride allowed the isolation of the major complex (**2**) in high diastereomeric purity (**2**:**3** ≥ 99:1, determined by HPLC). A fraction in which the diastereomer **3** gave precedence (**2**:**3** 11:89) could also be obtained. Both complexes are solid at room temperature (r.t.).

The structure of **2** was determined by X-ray diffraction of a single crystal. A perspective view of the molecule is shown in Fig. 2, which also gives some relevant atom numbers. Selected bond lengths and an-

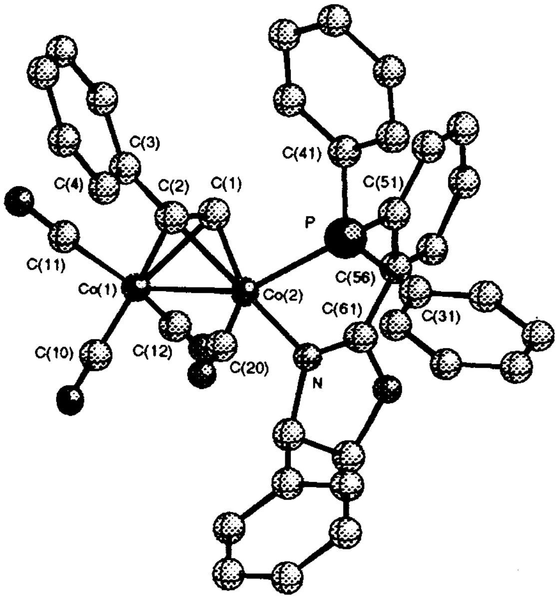


Fig. 2. Crystal structure of **2**. Hydrogen atoms have been omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for complex **1**

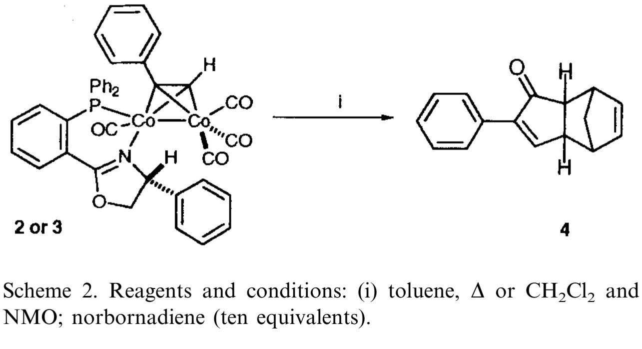
Bond lengths	
Co(1)–C(10)	1.739(10)
Co(1)–C(11)	1.775(8)
Co(1)–C(12)	1.782(9)
Co(1)–C(1)	1.957(7)
Co(1)–C(2)	1.997(7)
Co(1)–Co(2)	2.4899(15)
Co(2)–C(20)	1.790(7)
Co(2)–C(1)	1.926(7)
Co(2)–C(2)	1.898(7)
Co(2)–P	2.174(2)
Co(2)–N	2.014(5)
C(1)–C(2)	1.319(10)
Bond angles	
N–Co(2)–P	86.3(2)
C(20)–Co(2)–N	103.9(3)
C(1)–C(2)–C(3)	139.6(6)
C(41)–P–C(31)	102.4(3)
C(41)–P–C(51)	104.7(3)
C(31)–P–C(51)	102.3(3)
C(41)–P–Co(2)	121.1(2)
C(31)–P–Co(2)	118.6(2)
C(51)–P–Co(2)	105.5(2)
Torsional angles	
C(51)–C(56)–C(61)–N	22.2(11)
C(56)–C(61)–N–Co(2)	11.7(11)
P–Co(2)–N–C(61)	−46.9(6)
N–Co(2)–P–C(51)	52.5(3)
Co(2)–P–C(51)–C(56)	−42.5(5)
P–C(51)–C(56)–C(61)	0.2(9)
C(1)–C(2)–C(3)–C(4)	−162.4(9)

gles in the complex are given in Table 1. The most significant feature of **2** is the simultaneous coordination to one of the cobalts of the phosphorus and of the nitrogen atoms. The observed Co(1)–Co(2) bond length, 2.49 Å, is close to those found in other similar complexes with bulky ligands [15]. The cobalt–nitrogen and cobalt–phosphorus distances are 2.01 and 2.17 Å, respectively. The cobalt–CO distances fall in the range 1.73–1.79 Å, typical of $[Co_2(\mu\text{-}R^1CCR^2)L_2(CO)_4]$ complexes [5c]. Complex **2** is the first example of an alkyne-dicobaltcarbonyl complex containing a chiral bidentate ligand. In particular, the coordination of a cobalt cluster atom with the dihydrooxazole nitrogen has not been described until now; in fact, heating a toluene solution of the phenylacetylene dicobalthexacarbonyl complex in the presence of (*S*)-4-isobutyl-2-phenyl-4,5-dihydrooxazole did not lead to the formation of a stable complex. The pro-*R* cobalt atom (Co(2)) is coordinated both with the phosphorus atom on the pseudoaxial site, and with the nitrogen atom on the pseudoequatorial site that places the dihydrooxazole moiety close to the unsubstituted end (C(1)) of the alkyne moiety. Examination of molecular models shows that a similar coordination mode of the ligand with the pro-*S* cobalt atom (Co(1)) would lead to an increase of the steric interactions of the dihydrooxazole substituent at C(4) with the cobalt–CO cluster.

This complex appears to be very stable; a hexane solution of **2** showed no signs either of decomposition or of conversion to **3** after 2 days at r.t., as evidenced by HPLC analysis. It is worth noting that the diastereomeric complexes resulting from triphenylphosphine substitution on chiral dicobalthexacarbonylpropargylic alcohol complexes undergo a significant amount of isomerization under similar conditions ($t_{1/2}$ = 50–200 h) [16]. On the other hand, a hexane solution of a 3.1:1 **3**:**2** mixture showed extensive decomposition (85%) of **3** after 2 days at r.t., although no conversion to **2** had taken place. The enhanced stability of **2** and **3** towards interconversion processes appears therefore to be related to their chelated structure. The fast decomposition of the minor complex **3** precluded its complete characterization. Nevertheless, evidence for the assumption of the coordination of phosphorous and nitrogen in complex **3** comes from the fact that the C=N stretching band in the IR spectra of both **2** and **3** appears at the same frequency (1625 cm^{-1}) [17]. The ^{31}P-NMR spectra of both **2** and **3** were identical, showing a sharp singlet at 57.1 ppm [18].

Another unprecedented feature of **2** is the high diastereoselectivity observed in its formation. Although in ligand **1** the stereogenic center is farther from phosphorus than in (*R*)-(+)-glyphos, the nitrogen–cobalt coordination brings the stereogenic center close to the Co_2C_2 cluster, allowing an efficient discrimination between the two enantiotopic cobalt atoms. In particular, the phenyl substituent of the dihydrooxazole, that is only two bonds away from a cobalt atom, could produce a steric effect higher than that exerted by (*R*)-(+)-glyphos, that places its stereogenic center three bonds away from cobalt in the corresponding complexes [10].

We have also briefly investigated the Pauson–Khand reactivity of the new complexes **2** and **3** (Scheme 2 and Table 2). The major diastereomer reacted with norbornadiene to give the corresponding dextrorotatory Pauson–Khand adduct (+)-**4** with almost quantitative yield and in 51% ee (Entry 1). Upon activation of the reaction with *N*-methylmorpholine *N*-oxide at r.t. under oxygen atmosphere, the enantioselectivity decreased



Scheme 2. Reagents and conditions: (i) toluene, Δ or CH_2Cl_2 and NMO; norbornadiene (ten equivalents).

Table 2
Intermolecular Pauson–Khand reaction of complexes **1** and **2**

Entry	Initial complex (de) [a] (%)	Reaction conditions (solvent, temperature, atmosphere)	Yield (%)	Product [b] (ee) [c] (%)
1	**2** (97.3)	Toluene, 60°C, N_2	99	(+)-**4** (51)
2	**2** (97.3)	CH_2Cl_2, NMO (6 equiv.), r.t., O_2	94	(+)-**4** (6)
3	**2** (97.3)	CH_2Cl_2, NMO (6 equiv.), r.t., N_2	83	(+)-**4** (9)
4	**3** (79.2)	Toluene, 60°C, N_2	91	(−)-**4** (57)

[a] Conditions for the determination of the diastereomeric purity of **2** and **3** by HPLC analysis: Chiralcel OD (25 cm) column, 1% isopropyl alcohol 99% hexane, 0.5 ml min^{-1}, 30°C, $\lambda = 254$ nm, $P = 14$ bar. t_R(**2**): 17.9 min; t_R(**3**): 17.3 min.

[b] The symbols (+) and (−) refer to the sign of $[\alpha]_D^{23}$ for adduct **4**, measured in methylene chloride solution.

[c] Conditions for the determination of the enantiomeric purity of **4** by HPLC analysis: Chiralcel OD (25 cm) column, 2% isopropyl alcohol–98% hexane, 0.5 ml min^{-1}, 30°C, $\lambda = 254$ nm, $P = 14$ bar. t_R((−)-**4**): 20.6 min; t_R((+)-**4**): 16.5 min.

dramatically (6% ee) (Entry 2). In order to check the possibility that the observed enantioselectivity decrease was due to oxidation of the ligand under these conditions, the reaction was run under nitrogen (Entry 3), but only a marginal increase in the enantioselectivity was recorded. The minor diastereomer **3** (79.2% de) reacted with norbornadiene under thermal conditions to give the levorotatory cyclopentenone (−)-**4** in 57% ee (Entry 4).

The preparation of new alkyne-dicobaltcarbonyl complexes derived from other chiral 2-(2-phosphinoaryl)dihydrooxazoles, as well as their application in inter- and intramolecular Pauson–Khand reactions, are currently being investigated in our laboratories.

3. Experimental

3.1. General and analytical methods

Melting points were determined in an open capillary tube and are uncorrected. Optical rotations were measured on a Perkin–Elmer 241 MC polarimeter. Concentrations are given in g 100 ml^{-1}. IR spectra were recorded in FT mode, using film (NaCl) or KBr pellet techniques. The ^{1}H-NMR spectra were recorded at 500 MHz and ^{13}C-NMR spectra were recorded at 75.4 MHz. Chemical shifts are given in ppm and referenced to TMS or $CHCl_3$. The ^{31}P-NMR spectra were recorded at 121.4 MHz, chemical shifts are given in ppm and using phosphoric acid as an external reference. *J* values are given in Hz. Signal multiplicities were established by DEPT experiments. Exact mass measurements (HRMS) were performed by the Servicio de Espectroscopía de Masas de la Universidad de Córdoba. All reactions were performed in flame or oven-dried glassware under a N_2 atmosphere. Reaction progress was followed by TLC (Merck DC-Alufolien Kieselgel 60 F254). Silica gel (70–230 mesh) was used for column chromatography. Phenylacetylene dicobalthexacarbonyl complex [1] and (−)-(*R*)-2-(2-diphenylphosphinophenyl)-4-phenyl-4,5-dihydrooxazole **1** [14] were prepared as previously described.

3.2. Preparation of complex **2**

To a solution of the phenylacetylene dicobalthexacarbonyl complex (533 mg, 1.376 mmol) in toluene (15 ml) was added solid (−)-(*R*)-2-(2-diphenylphosphinophenyl)-4-phenyl-4,5-dihydrooxazole (**1**) (554 mg, 1.363 mmol) in a single portion. The reaction mixture was heated to 60°C for 2 h, after which time TLC analysis showed only a trace of the starting complex. The reaction mixture was partially concentrated by evaporation of the solvent at reduced pressure and the remaining mixture was filtered through a short pad of silica gel previously washed with ether and hexane. Evaporation of the solvent afforded a solid residue (766 mg, 76% yield) containing a 85:15 mixture (70% de) of two diastereomers **2**:**3**, as determinated by HPLC. Fractional recrystallization of the mixture from hexane–methylene chloride (12.5:1) allowed the isolation of three enriched fractions: (a) 240 mg of pure ($\geq 98\%$ de) **2** as a brown crystalline solid; (b) 351 mg of a 88:12 **2**:**3** mixture and (c) 42 mg of a 11:89 **2**:**3** mixture.

Complex **2**: brown crystalline solid. M.p. (dec.): 157–160°C. $[\alpha]_D = +478$ ($c = 0.0142$, C_6H_6). IR (KBr): $\nu = 2020$, 1964, 1954, 1927, 1625, 1591 cm^{-1}. ^{1}H-NMR: δ (ppm) 4.32 (dd, $J = 8.5$ and 6 Hz, 1H), 4.69 (t, $J = 9$ Hz, 1H), 4.83 (dd, $J = 10$ and 5.5 Hz, 1H), 5.56 (d, $J = 6$ Hz, 1H), 6.80–6.72 (m, 2H), 6.90–7.02 (m, 7H), 7.02–7.08 (m, 1H), 7.08–7.22 (m, 7H), 7.26–7.34 (m, 3H), 7.43 (t, $J = 6.8$ Hz, 1H), 7.51 (t, $J = 7.4$ Hz, 1H), 7.63 (t, $J = 7.4$ Hz, 1H), 8.16–8.21 (m, 1H). ^{13}C-NMR: δ (ppm) 69.6 (CH, acetylenic), 74.7, 74.5, 86.7 (C_q), 125.1 (CH), 127.5–132.0 (unresolved set of signals, C–Ar and CH–Ar), 132.2 (d, $J_{C-P} = 14$ Hz, 1C_q), 133.2 (d, $J_{C-P} = 15$ Hz, 1C_q), 127–135 (m), 140.0 (C_q), 142.1 (Cq), 164.4 (C_q, C=N), 203.6 (s, broad, 3CO), 208.1 (s, CO). ^{31}P-NMR: δ (ppm) +57.1. FAB$^+$ MS $m/e = 739.2$ (M, 2%), 711.2 (M − CO, 12%), 627.3 (M − 4CO, 100%). FAB$^+$

HRMS Calc. for $C_{35}H_{28}Co_2NOP$ (M − 4CO): 627.053. Found: 627.057.

*3.3. X-ray structure determination and refinement of complex **2***

3.3.1. Crystal data

Suitable crystals were grown from a 12.5:1 hexane–methylene chloride solution. $C_{39}H_{28}NO_5PCo_2$, $M_r = 739.45$. Orthorhombic; $a = 12.071(6)$, $b = 15.927(10)$, $c = 18.390(10)$ Å, $V = 3536(3)$ (by least-squares refinement on diffractometer angles for 25 automatically centered reflections), space group $P2_12_12_1$ (no. 19), $Z = 4$, $D_{calc} = 1.389$ g cm^{-3}. Brown, air-stable crystals, μ (Mo–K_α) = 1.03 mm^{-1}.

3.3.2. Data collection and processing

Data were collected on an Enraf–Nonius CAD4 diffractometer using graphite-monochromated Mo–K_α radiation ($\lambda = 0.71069$ Å) and a $\omega - 2\theta$ scan, ω scan width = $0.80 + 0.35 \tan\theta$, ω scan speed 1.3–5.5°. Reflection ranges for the data collection were $1° < \theta < 25°$, $0 \leq h \leq 14$, $0 \leq k \leq 18$, $0 \leq l \leq 21$. Lp and empirical absorption corrections [19] were applied, $T_{min} = 0.722$, $T_{max} = 1.000$. Unique reflections, 3094; 2394 with $I > 2\sigma(I)$.

3.3.3. Structure analysis and refinement

The structure was solved by direct methods (SHELXS-86) [20] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97) [21]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions with isotropic temperature factors 0.5 times the U_{eq} values of corresponding carbons (see Table 3). The weighting scheme was $w = 1/[\sigma^2(F_o^2) + (0.0681P)^2]$ where $P = [\max.\ (F_o^2, 0) + 2F_c^2]/3$. Final $R(F)$ and $Rw(F^2)$ values were 0.045 and 0.101 for reflections with $I > 2\sigma(I)$.

*3.4. Preparation of (+)-**4***

1. Thermal reaction. To a stirred solution of complex **2** (97.3% de) (65 mg, 0.088 mmol) in toluene (3 ml) norbornadiene (80 mg, 0.88 mmol) was added dropwise. The resulting solution was heated for 18 h at 60°C until complete disappearance of the starting material (TLC). The reaction mixture was cooled to r.t. and filtered through Celite, which was thoroughly washed with dichloromethane. The solvents were eliminated under reduced pressure, and the crude product was purified by column chromatography on silica gel, eluting with hexane–ethyl acetate mixtures of increasing polarity, to give 19 mg (99%) of the enone (+)-**4** (51% ee).
2. *N*-Oxide-promoted reaction. To a stirred solution of complex **2** (97.3% de) (22 mg, 0.029 mmol) in dry dichloromethane (1.5 ml), under oxygen atmosphere at r.t., were added norbornadiene (22 mg, 0.238 mmol) and solid *N*-methylmorpholine *N*-oxide (21 mg, 0.178 mmol) in one portion. Although the reaction was complete after 48 h, as shown by TLC,

Table 3
Atomic coordinates (×10^4) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for **2**

Atom	*x*	*y*	*z*	U_{eq} [a]
Co(1)	350(1)	3109(1)	7019(1)	51(1)
C(10)	316(7)	2114(6)	7407(4)	66(2)
O(10)	281(6)	1453(4)	7694(3)	90(2)
C(11)	−816(8)	3156(6)	6432(4)	71(2)
O(11)	1545(7)	3218(6)	6055(5)	129(3)
C(12)	1450(8)	3167(6)	6374(4)	69(2)
O(12)	2154(6)	3258(6)	5982(4)	119(3)
Co(2)	1292(1)	3633(1)	8135(1)	42(1)
C(20)	1228(6)	2826(5)	8810(4)	51(2)
O(20)	1087(5)	2333(4)	9244(3)	71(2)
C(1)	479(7)	4249(4)	7407(4)	50(2)
C(2)	−193(6)	3824(4)	7837(3)	45(2)
C(3)	−1335(6)	3863(4)	8112(4)	48(2)
C(4)	−1663(7)	3414(6)	8712(4)	66(2)
C(5)	−2717(8)	3480(7)	8979(5)	85(3)
C(6)	−3467(8)	3992(7)	8661(7)	96(3)
C(7)	−3179(7)	4440(6)	8055(8)	98(3)
C(8)	−2114(7)	4380(6)	7779(5)	81(3)
P	1819(2)	4729(1)	8749(1)	43(1)
C(31)	2904(6)	4603(4)	9429(3)	51(2)
C(32)	2743(8)	4039(5)	9995(4)	71(2)
C(33)	3533(10)	3940(7)	10 533(5)	91(3)
C(34)	4455(9)	4424(7)	10 525(5)	88(3)
C(35)	4633(7)	4979(8)	9976(5)	89(3)
C(36)	3841(7)	5078(6)	9436(4)	72(2)
C(41)	826(5)	5383(4)	9217(3)	51(2)
C(42)	−208(5)	5503(5)	8924(4)	62(2)
C(43)	−1001(7)	5977(5)	9268(5)	75(2)
C(44)	−776(8)	6332(7)	9927(5)	97(3)
C(45)	240(10)	6206(10)	10 231(6)	158(7)
C(46)	1022(8)	5723(7)	9891(5)	104(4)
C(51)	2472(5)	5424(4)	8089(3)	45(1)
C(52)	2301(6)	6264(4)	8078(4)	54(2)
C(53)	2776(7)	6770(5)	7553(5)	70(2)
C(54)	3487(6)	6433(5)	7046(4)	69(2)
C(55)	3690(6)	5607(5)	7055(4)	62(2)
C(56)	3200(5)	5067(4)	7554(4)	48(2)
C(61)	3423(6)	4187(5)	7524(4)	50(2)
N(62)	2861(4)	3575(4)	7767(3)	46(1)
C(63)	3403(6)	2772(4)	7590(4)	57(2)
C(64)	4487(7)	3083(6)	7245(5)	78(3)
O(65)	4390(4)	3969(4)	7174(3)	64(2)
C(71)	3569(6)	2199(4)	8224(3)	49(2)
C(72)	3258(7)	1386(5)	8180(5)	69(2)
C(73)	3433(9)	841(6)	8758(5)	87(3)
C(74)	3958(8)	1123(7)	9380(5)	85(3)
C(75)	4258(7)	1927(6)	9419(4)	75(2)
C(76)	4085(6)	2479(6)	8856(4)	63(2)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

the reaction was left to proceed overnight so that the violet Co precipitate settled out. The reaction mixture was filtered through Celite, which was thoroughly washed with methylene chloride. The solvents were eliminated under reduced pressure, and the crude product was purified by column chromatography on silica gel eluting with hexane–ethyl acetate mixtures of increasing polarity to give 6 mg (94% yield) of (+)-**4** (6% ee). When the reaction was performed under the same conditions under an atmosphere of dry nitrogen, very similar results were obtained (see Table 2).

3.5. Preparation of (−)-4

The procedure described above for the thermal reaction was used, with the following reagents, conditions and quantities: 22 mg (0.029 mmol) of **3** (79.3% de) and 27 mg (0.297 mmol) of norbornadiene in 1.5 ml of toluene. The reaction was conducted at 60°C for 18 h and gave 6 mg (91% yield) of (−)-**4** (57% ee). The spectral data of compound **4** are identical to those described in Ref. [22].

Acknowledgements

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References

[1] H. Greenfield, H.W. Stenberg, R.A. Friedel, J.H. Wotiz, R. Markby, I. Wender, J. Am. Chem. Soc. 76 (1954) 1457.

[2] (a) R.S. Dickson, P.J. Frasa, Adv. Organomet. Chem. 12 (1974) 323. (b) N.E. Schore, Chem. Rev. 88 (1988) 1081.

[3] (a) K.M. Nicholas, R. Pettit, Tetrahedron Lett. (1971) 3475. (b) D. Seyferth, M.O. Nestle, A.T. Wehman, J. Am. Chem. Soc. 97 (1975) 7417.

[4] (a) K.M. Nicholas, Acc. Chem. Res. 20 (1987) 207. (b) N.E. Schore, S.D. Najdi, J. Org. Chem. 52 (1987) 5296. (c) T. Nagasawa, K. Taya, M. Kitamura, K. Suzuki, J. Am. Chem. Soc. 118 (1996) 8949. (d) S. Dare, B. Ducroix, S. Bernard, K.M. Nicholas, Tetrahedron Lett. 37 (1996) 4341. (e) N.E. Schore, Org. React. 40 (1991) 1.

[5] (a) D.H. Bradley, M.A. Khan, K.M. Nicholas, Organometallics 11 (1992) 2598. (b) J.C. Jeffery, R.M.S. Pereira, M.D. Vargas, M.J. Went, J. Chem. Soc. Dalton Trans. (1995) 1805. (c) J.-J. Bonnet, R. Mathieu, Inorg. Chem. 17 (1978) 1973.

[6] (a) A. Gelling, M.J. Wend, J. Organomet. Chem. 455 (1993) 203. (b) K. Yang, S.G. Bott, M.G. Richmond, J. Organomet. Chem. 516 (1996) 65. (c) A. Gelling, J.C. Jeffery, D.C. Povey, M.J. Went, J. Chem. Soc. Chem. Commun. (1991) 349. (d) H.A. Mirza, J.J. Vittal, R.J. Puddephatt, C.S. Frampton, L. Manojlovic-Muir, W. Xia, R.H. Hill, Organometallics 12 (1993) 2767.

[7] R. Rumin, L. Manojlovic-Muir, K.W. Muir, F.Y. Pétillon, Organometallics 7 (1988) 375.

[8] M. Arewgoda, B.H. Robinson, J. Simpson, J. Am. Chem. Soc. 105 (1983) 1893.

[9] A.J. Edwards, S.R. Mack, M.J. Mays, C.-Y. Mo, P.R. Raithby, M.-A. Rennie, J. Organomet. Chem. 519 (1996) 243.

[10] (a) P. Bladon, P.L. Pauson, H. Brunner, R. Eder, J. Organomet. Chem. 355 (1988) 449. (b) A.M. Hay, W.J. Kerr, G.G. Kirk, D. Middlemiss, Organometallics 14 (1995) 4986.

[11] For an alternative preparation of alkyne-pentacarbonylphosphinedicobalt complexes, see: J.C. Anderson, B.F. Taylor, C. Viney, G.J. Wilson, J. Organomet. Chem. 519 (1996) 103.

[12] (a) J. Castro, H. Sörensen, A. Riera, C. Morin, A. Moyano, M.A. Pericàs, A.E. Greene, J. Am. Chem. Soc. 112 (1990) 9388. (b) H.-J. Park, B.Y. Lee, Y.K. Kang, Y.K. Chung, Organometallics 14 (1995) 3104. (c) S. Fonquerna, A. Moyano, M.A. Pericàs, A. Riera, J. Am. Chem. Soc. 119 (1997) 10225, and Refs. cited therein.

[13] (a) P. von Matt, A. Pfaltz, Angew. Chem. Int. Ed. Engl. 32 (1993) 566. (b) J. Spinz, G. Helmchen, Tetrahedron Lett. 34 (1993) 1769. (c) J.M.J. Williams, Synlett (1996) 705. (d) D. Carmona, C. Cativiela, S. Elipe, F.J. Lahoz, M.P. Lamata, M.P. López-Ram de Víu, L.A. Oro, C. Vega, F. Viguri, Chem. Commun. (1997) 2351.

[14] M. Peer, J.C. de Jong, M. Kiefer, T. Langer, H. Rieck, H. Schell, P. Sennhenn, J. Sprinz, H. Steinhagen, B. Wiese, G. Helmchen, Tetrahedron 52 (1996) 7547.

[15] (a) P.H. Bird, A.R. Fraser, D.N. Hall, Inorg. Chem. 16 (1977) 1923. (b) C. Bianchini, P. Dapporto, A. Meli, J. Organomet. Chem. 174 (1979) 205.

[16] D.H. Bradley, M.A. Khan, K.M. Nicholas, Organometallics 8 (1989) 554.

[17] (Diphenylphosphinophenyl)oxazoline-containingalkyne-dicobaltcarbonyl complexes in which the nitrogen atom is not bound to cobalt have also been prepared in our laboratories and show higher frequencies for this band (1647–1665 cm^{-1}). This behavior is in complete accordance with the observations by Pfaltz and co-workers, who describe a similar shift (from 1645 to 1624 cm^{-1}) of the C=N stretching band upon chelation of the phosphinooxazoline **1** with Zn(II): G. Koch, G.C. Lloyd-Jones, O. Loiseleur, A. Pfaltz, R. Prétôt, S. Schaffner, P. Schnider, P. von Matt, Recl. Trav. Chim. Pays-Bas 114 (1995) 206.

[18] The insensitivity of the ^{31}P chemical shifts to different environments in chiral phosphine-substituted acetylene-dicobaltcarbonyl complexes is well known: M.F. D'Agostino, C.S. Frampton, M.J. McGlinchey, Organometallics 9 (1990) 2972.

[19] A.C.T. North, P.C. Philips, F.S. Mathews, Acta Crystallogr. A 24 (1968) 351.

[20] G.M. Sheldrick, SHELXS-86, in: G.M. Sheldrick, C. Krüger, R. Goddard (Eds.), Crystallographic Computing 3, Oxford University Press, Oxford, UK, 1985, pp. 175–178.

[21] G.M. Sheldrick, SHELXS-97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1992.

[22] I.U. Khand, G.R. Knox, P.L. Pauson, W.E. Watts, M.I. Foreman, J. Chem. Soc. Perkin Trans. I (1973) 977.