

# Preparation and crystal structures of a bidentate isocyanide and its tetracarbonylchromium complex<sup>1</sup>

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## Abstract

The bidentate diisocyanide ligand 2,2'-(methylenedioxy)diphenylisocyanide **4** was prepared by Williamson coupling of 2-nitrophenol with dichloromethane, reduction of the nitro functions and conversion of the primary amine groups into isocyanide functions in Ugi synthesis. The novel ligand **4** reacts with  $[M(\text{nor})(\text{CO})_4]$  (nor = norbornadiene) to yield the complexes  $[M(\mathbf{4})(\text{CO})_4]$  (M = Cr, **5**; M = Mo, **6**) which possess 12-membered chelate rings, the smallest rings observed so far for chelating isocyanide ligands. Compounds **4** and **5** were characterized by X-ray crystallography.

**Keywords:** Bidentate diisocyanide; Chromium complex; Molybdenum complex; X-ray crystallography

## 1. Introduction

The chemistry of multidentate isocyanides has recently attracted some interest owing to their potential use in nuclear medicine for the complexation of <sup>99m</sup>Tc [1,2] and their interesting coordination chemistry [3]. We reported recently on the coordination chemistry of tripodal aromatic (A [4], B [5], C [6], D [6]) and aliphatic (E [7], F [7]) triisocyanides (Fig. 1).

In spite of the linear M–C≡N–R unit in metal complexes and the associated geometric constraints, the tripodal triisocyanides can form mononuclear chelate complexes. However, large chelate rings are obtained with these ligands, which are composed of 12 (for complexes of E and F) to 20 (for complexes of B) atoms. The smallest ring obtained so far with a tripodal aromatic triisocyanide contains 14 atoms (complex of D [6]), while the more flexible aliphatic tripodal triisocyanides can form chelate rings with only 12 atoms.

In order to find the smallest backbone for the formation of chelate complexes with aromatic isocyanides, we investigated the coordination chemistry of the ligand **4** (Scheme 1). If it forms a chelate complex a ring with

only 12 atoms will be obtained, the smallest so far for an aromatic polyisocyanide. These studies were encouraged by reports by Angelici and coworkers [8] about a bidentate aromatic diisocyanide forming 13-membered chelate rings with Rh(I) and by reports on aliphatic diisocyanides capable of forming 12-membered chelate rings with Rh(I) [9].

## 2. Experimental section

All operations were performed in an atmosphere of dry argon using Schlenk and vacuum techniques. All solvents were dried by standard methods and distilled prior to use. <sup>1</sup>H NMR spectra and <sup>13</sup>C NMR spectra were recorded on a Bruker AM 250 NMR spectrometer. Infrared spectra were taken in KBr on a Perkin–Elmer 983 instrument. Elemental analyses (C, H, N) were performed on a Vario EL elemental analyzer at the Freie Universität Berlin. Mass spectra were recorded on Finnigan MAT 112 or Finnigan MAT 711 instruments. Complexes  $[M(\text{nor})(\text{CO})_4]$  (nor = norbornadiene, M = Cr, Mo) were obtained as described [10].

### 2.1. Bis(2-nitrophenoxy)methane (1)

30 g (216 mmol) of 2-nitrophenol and 9.16 g (108 mmol) of dichloromethane were dissolved in 200 ml

<sup>1</sup> Dedicated to Prof. Dr. Walter Siebert on the occasion of his 60th birthday.

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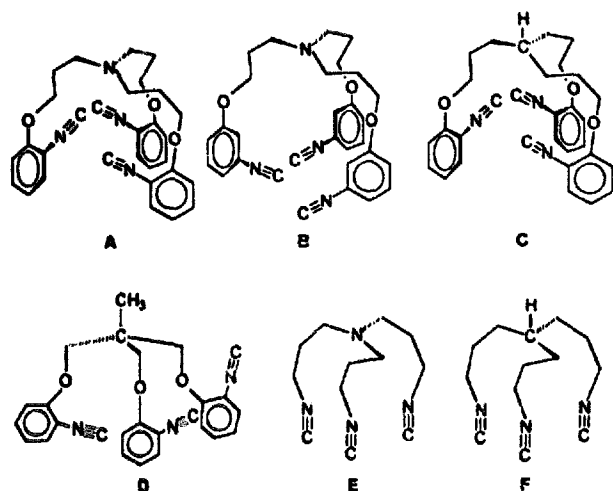
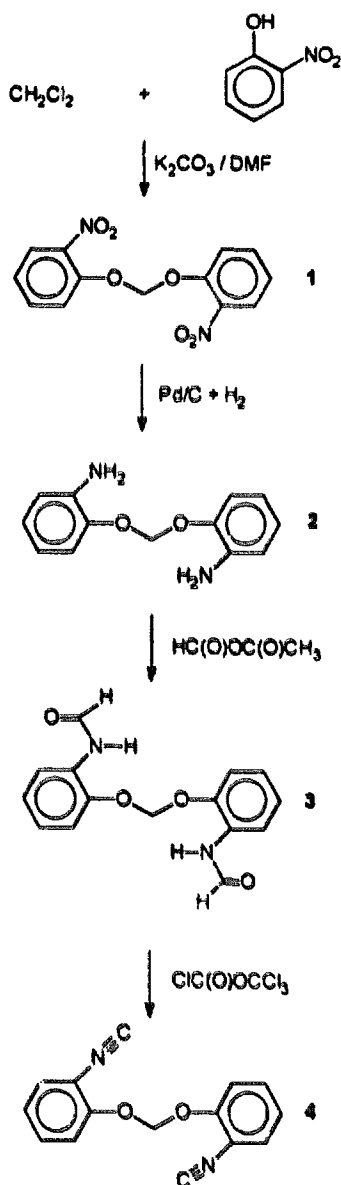


Fig. 1. Topology of tripodal trisocyanide ligands.



Scheme 1. Preparation of the diisocyanide 4.

of DMF. A 30 g (217 mmol) sample of  $K_2CO_3$  was added to the solution. The mixture was heated under reflux for 35 min. After cooling to room temperature the reaction mixture was added to 1 l of ice-water. Filtration of this mixture yielded a white solid which was washed with ethanol and ether. Recrystallization from methanol/acetone gave **1** as white needles (27.8 g, 89%). Anal. Found: C, 53.93; H, 3.54; N, 8.54.  $C_{13}H_{10}N_2O_6$  ( $M = 290.23$ ) Calc.: C, 53.80; H, 3.47; N, 9.65%.  $^1H$  NMR (250 MHz,  $CDCl_3$ ):  $\delta$  7.97–7.07 (m, 8H, Ar-H), 5.95 (s, 2H,  $OCH_2O$ ).  $^{13}C$  NMR (62.9 MHz,  $CDCl_3$ ):  $\delta$  149.35, 140.64, 134.19, 125.35, 122.89, 117.45 (Ar-C), 91.76 ( $OCH_2O$ ).

### 2.2. 2,2'-(Methylenedioxy)bis(phenylamin) (2)

A 10 g (34 mmol) sample of **1** was dissolved in 100 ml of THF. To this solution was added 100 mg of Pd/C hydrogenation catalyst (10% Pd, Aldrich). The reaction mixture was stirred in an autoclave under  $H_2$  (120 bar) for 12 h. Subsequently the catalyst was separated by filtration and the THF was stripped in vacuo leaving the diamine **2** as colorless powder. Yield 4.91 g (62%). Anal. Found: C, 67.37; H, 6.21; N, 12.06.  $C_{13}H_{14}N_2O_2$  ( $M = 230.27$ ) Calc.: C, 67.81; H, 6.13; N, 12.17%.  $^1H$  NMR (250 MHz,  $CDCl_3$ ):  $\delta$  7.43–7.77 (m, 8H, Ar-H), 5.91 (s, 2H,  $OCH_2O$ ), 3.97 (s, 4H,  $NH_2$ ).  $^{13}C$  NMR (62.9 MHz,  $CDCl_3$ ):  $\delta$  144.39, 137.36, 123.24, 118.33, 115.68, 115.43 (Ar-C), 92.74 ( $OCH_2O$ ).

### 2.3. *N,N'*-(methylenebis(oxy-1,2-phenylene))diacetamide (3)

4.91 g (21 mmol) of **2** was dissolved in 200 ml of ether and 4 ml of acetic-formic anhydride was added dropwise. The reaction mixture was stirred at room temperature for 2 h. All volatile materials were then removed at a rotary evaporator. The resulting white powder was washed with ether and pentane. The compound can be recrystallized from THF giving **3** as white crystals. Yield 5.46 g (92%). Anal. Found: C, 62.08; H, 4.94; N, 9.56.  $C_{15}H_{14}N_2O_4$  ( $M = 286.29$ ) Calc.: C, 62.93; H, 4.93; N, 9.79%.

### 2.4. 2,2'-(Methylenedioxy)diphenylisocyanid (4)

A 5.46 g (20 mmol) sample of **3** in 100 ml of  $CH_2Cl_2$  and 12 ml of  $NEt_3$  was mixed in a three-necked round-bottomed flask equipped with argon inlet, magnetic stirrer, thermometer, condenser and rubber septum. The mixture was cooled to  $-78^\circ C$  and 2.5 ml diphosgene was added via the septum with a syringe. The brown solution was allowed to warm to room temperature and was stirred for an additional 12 h. The reaction mixture

was then washed once with 100 ml of water and twice with an aqueous  $\text{Na}_2\text{CO}_3$  solution (10%). The brown dichloromethane solution was then dried with  $\text{Na}_2\text{SO}_4$ , and the solvent was removed in vacuo. The resulting brown oil was purified chromatographically on  $\text{Al}_2\text{O}_3$  (4%  $\text{H}_2\text{O}$ ) with dichloromethane as eluent giving colorless crystals, 4.34 g (88%), of **4**. Anal. Found: C, 71.28; H, 3.72; N, 10.87.  $\text{C}_{15}\text{H}_{10}\text{N}_2\text{O}_2$  ( $M = 250.26$ ) Calc.: C, 71.99; H, 4.03; N, 11.19%. IR (KBr):  $\nu = 2127\text{ cm}^{-1}$  (s, CN).  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.49–6.95 (m, 8H, Ar-H), 5.95 (s, 2H,  $\text{OCH}_2\text{O}$ ).  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  169.16 (br, Ar-NC), 152.24, 131.01, 128.26, 123.40 (Ar-C), 117.75 (br, Ar-C-NC), 116.15 (Ar-C), 91.66 ( $\text{OCH}_2\text{O}$ ).

### 2.5. *cis*-[Cr(4)(CO)<sub>4</sub>] (5)

Solutions of **4** (488 mg, 2.0 mmol) in 50 ml of  $\text{CH}_2\text{Cl}_2$  and [Cr(nor)(CO)<sub>4</sub>] (500 mg, 2.0 mmol) in 50 ml of  $\text{CH}_2\text{Cl}_2$  were added simultaneously over 5 h to 20 ml of dichloromethane. The mixture was stirred at room temperature for 12 h. All solvents were then removed and the yellow residue was washed with hexane (removal of  $\text{C}_7\text{H}_8$ ) and dried in vacuo. The product was purified by recrystallization from dichloromethane/hexane. Yield 465 mg (56%). Anal. Found: C, 54.51; H, 3.03; N, 6.85.  $\text{C}_{19}\text{H}_{10}\text{CrN}_2\text{O}_6$  ( $M = 414.30$ ) Calc.: C, 55.08; H, 2.43; N, 6.76%. IR (KBr):  $\nu = 2137$  (m, CN), 2082 (m, CN),

2005 (s, CO), 1950 (s sh, CO), 1925 (vs, CO),  $1902\text{ cm}^{-1}$  (vst, CO).  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.41–6.92 (m, 8H, Ar-H), 5.70 (s, 2H,  $\text{OCH}_2\text{O}$ ).  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  220.74 (*cis*, *trans* CO), 217.68 (*cis*, *cis* CO), 184.36 (Ar-NC), 153.90, 129.87, 126.14, 124.29 (Ar-C), 121.65 (br, Ar-C-NC), 118.56 (Ar-C), 98.12 ( $\text{OCH}_2\text{O}$ ). MS (EI, 80 eV,  $m/z$ , rel. int.): 414 ( $\text{M}^+$ , 14), 330 ( $\text{M}^+ - 3\text{CO}$ , 21), 302 ( $\text{M}^+ - 4\text{CO}$ , 100), 183 ( $\text{C}_8\text{H}_5\text{NOCr}^+$ , 13), 170 ( $\text{C}_7\text{H}_4\text{NOCr}^+$ , 63), 52 ( $\text{Cr}^+$ , 84).

### 2.6. *cis*-[Mo(4)(CO)<sub>4</sub>] (6)

The preparation of **6** is analogous to the procedure for **5** from 381 mg (1.5 mmol) **4** and 457 mg [Mo(nor)(CO)<sub>4</sub>]. Complex **6** was obtained as yellowish crystals in 48% yield (330 mg). Anal. Found: C, 49.89; H, 2.54; N, 6.06.  $\text{C}_{19}\text{H}_{10}\text{MoN}_2\text{O}_6$  ( $M = 458.24$ ) Calc.: C, 49.80; H, 2.20; N, 6.11%. IR (KBr):  $\nu = 2145$  (m, CN), 2107 (m, CN), 2013 (s, CO), 1926 (vs, CO), 1903 (vs, CO),  $1889\text{ cm}^{-1}$  (vs, CO).  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.39–6.99 (m, 8H, Ar-H), 5.76 (s, 2H,  $\text{OCH}_2\text{O}$ ).  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  210.66 (*cis*, *trans* CO), 206.46 (*cis*, *cis* CO), 173.02 (Ar-NC), 153.80, 130.32, 126.50, 124.28 (Ar-C), 120.81 (br, Ar-C-NC), 118.51 (Ar-C), 98.00 ( $\text{OCH}_2\text{O}$ ). MS (EI, 80 eV,  $m/z$ , rel. int.): 460 ( $\text{M}^+$ , 0.42), 376 ( $\text{M}^+ - 3\text{CO}$ , 1.58), 348 ( $\text{M}^+ - 4\text{CO}$ , 21).

Table 1  
Selected crystal and data collection details for **4** and **5**

	<b>4</b>	<b>5</b>
Crystal size ( $\text{mm}^3$ )	0.44 × 0.42 × 0.35	0.74 × 0.64 × 0.32
Formula	$\text{C}_{15}\text{H}_{10}\text{N}_2\text{O}_2$	$\text{C}_{19}\text{H}_{10}\text{CrN}_2\text{O}_6$
Formula weight (amu)	250.26	414.30
<i>a</i> (Å)	9.591(3)	8.008(2)
<i>b</i> (Å)	9.591(3)	18.913(9)
<i>c</i> (Å)	13.431(6)	12.161(7)
$\alpha$ (°)	90.0	90.0
$\beta$ (°)	90.0	100.57(3)
$\gamma$ (°)	90.0	90.0
<i>V</i> (Å <sup>3</sup> )	1235(1)	1811(3)
Space group	$P4_1$ (No. 76)	$P2_1/c$ (No. 14)
<i>Z</i>	4	4
$D_{\text{calc}}$ ( $\text{g cm}^{-3}$ )	1.345	1.520
$D_{\text{obs}}$ ( $\text{g cm}^{-3}$ )	1.35	1.515
$\mu$ ( $\text{cm}^{-1}$ )	0.855	6.527
Radiation, $\lambda$ (Å)		Mo K $\alpha$ , 0.71073
2 $\theta$ Range (°)	$2 \leq 2\theta \leq 50$	
No. of unique data	1134	3190
No. of observed data, $F_o^2 \geq 3\sigma(F_o^2)$	919	2621
<i>R</i> (%) <sup>a</sup>	2.33	3.81
<i>R<sub>w</sub></i> (%) <sup>a</sup>	3.00	5.43
GOF <sup>a</sup>	1.087	1.345
No. of variables	171	254

<sup>a</sup> Estimated standard deviations are given in parentheses. For definition of residuals see Ref. [13].

Table 2  
Positional and equivalent isotropic thermal parameters for 4

Atom	x	y	z	$B_{eq}^a$ (Å <sup>2</sup> )
O1	0.4290(2)	-0.0105(1)	0.370	3.37(3)
O2	0.5107(1)	0.0710(1)	0.21611(9)	3.35(3)
N1	0.2503(2)	0.0014(2)	0.5199(1)	3.30(3)
N2	0.4989(2)	0.2497(2)	0.0659(1)	3.28(3)
C1	0.1703(2)	-0.0880(3)	0.5254(2)	4.48(5)
C2	0.3501(2)	0.1058(2)	0.5117(1)	3.03(4)
C3	0.4444(2)	0.1006(2)	0.4328(1)	2.96(4)
C4	0.5429(2)	0.2043(2)	0.4243(2)	3.80(4)
C5	0.5497(3)	0.3092(2)	0.4952(2)	4.32(5)
C6	0.4563(3)	0.3130(2)	0.5733(2)	4.20(5)
C7	0.3559(2)	0.2118(2)	0.5812(1)	3.57(4)
C8	0.5279(2)	-0.0280(2)	0.2929(2)	3.60(4)
C9	0.3992(2)	0.0559(2)	0.1530(1)	2.99(4)
C10	0.3944(2)	0.1498(2)	0.0740(1)	2.94(4)
C11	0.2883(2)	0.1439(2)	0.0044(1)	3.57(4)
C12	0.1873(2)	0.0431(3)	0.0124(2)	4.22(5)
C13	0.1915(2)	-0.0496(3)	0.0905(2)	4.40(5)
C14	0.2957(2)	-0.0428(2)	0.1612(2)	3.74(4)
C15	0.5880(3)	0.3295(2)	0.0603(2)	4.50(5)

$$^a B_{eq} = 8/3\pi^2[\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j].$$

### 2.7. X-ray crystal structure determinations

Crystals of 4 and 5 were grown at room temperature from dichloromethane or dichloromethane/hexane

(10:1, v/v) solutions respectively, and are air stable. Suitable specimens were selected in air and mounted at 20(2)°C on an Enraf–Nonius CAD4 diffractometer. Search and auto-indexing procedures gave a tetragonal

Table 3  
Positional and equivalent isotropic thermal parameters for 5

Atom	x	y	z	$B_{eq}^a$ (Å <sup>2</sup> )
Cr	0.20130(4)	0.21465(2)	0.23136(3)	3.908(7)
O1	0.1774(2)	0.00753(8)	0.3714(1)	5.00(3)
O2	0.0199(2)	-0.03814(8)	0.2172(1)	4.65(3)
O3	0.0202(3)	0.2995(1)	0.0375(2)	7.02(5)
O4	0.5286(3)	0.2358(1)	0.1444(2)	8.29(6)
O5	0.2793(3)	0.3427(1)	0.3784(2)	6.84(5)
O6	-0.1440(3)	0.1931(1)	0.2927(2)	6.86(5)
N1	0.3363(2)	0.12425(9)	0.4421(1)	4.43(4)
N2	0.1690(2)	0.06757(9)	0.1151(1)	4.37(4)
C1	0.2947(3)	0.1578(1)	0.3626(2)	4.25(4)
C2	0.3378(3)	0.0696(1)	0.5185(2)	3.95(4)
C3	0.2515(3)	0.0076(1)	0.4806(2)	4.08(4)
C4	0.2482(3)	-0.0475(1)	0.5549(2)	5.08(5)
C5	0.3315(3)	-0.0394(1)	0.6642(2)	5.47(5)
C6	0.4157(3)	0.0209(2)	0.6998(2)	5.48(6)
C7	0.4195(3)	0.0759(1)	0.6270(2)	4.73(5)
C8	0.0816(3)	-0.0523(1)	0.3290(2)	4.78(5)
C9	0.1247(3)	-0.0558(1)	0.1432(2)	3.77(4)
C10	0.1897(2)	-0.0022(1)	0.0859(2)	3.58(4)
C11	0.2778(3)	-0.0179(1)	0.0024(2)	4.27(4)
C12	0.3116(3)	-0.0872(1)	-0.0197(2)	5.04(5)
C13	0.2529(3)	-0.1403(1)	0.0396(2)	5.33(5)
C14	0.1578(3)	-0.1245(1)	0.1201(2)	4.77(5)
C15	0.1753(3)	0.1233(1)	0.1535(2)	4.30(4)
C16	0.0912(3)	0.2667(1)	0.1090(2)	4.65(5)
C17	0.4086(3)	0.2269(1)	0.1801(2)	5.38(5)
C18	0.2473(3)	0.2952(1)	0.3213(2)	4.47(5)
C19	-0.0135(3)	0.2009(1)	0.2712(2)	4.51(5)

$$^a B_{eq} = 8/3\pi^2[\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j].$$

cell for **4** and a monoclinic cell for **5**. Important crystal and data collection details are listed in Table 1. Diffraction data were collected at 20(2)°C using  $\omega$ -2 $\theta$  scans. Raw data were reduced to structure factors (neutral scattering factors were used, terms of anomalous dispersion from Ref. [11], Table 2.3.2.) (and their e.s.d.s) by correcting for scan speed, Lorentz and polarization effects. An empirical absorption correction based on six  $\Psi$  scans was applied to the data for **5**. The space group was unambiguously determined to be  $P2_1/c$  for **5** and was assumed to be  $P4_1$  for **4**. Solution and refinement of the structure of **4** confirmed this choice. Both structures were solved by direct methods. The positional parameters for all non-hydrogen atoms were refined by using first isotropic and later anisotropic thermal parameters. Difference Fourier maps calculated after refinement with anisotropic thermal parameters showed almost all hydrogen positions. However, hydrogen atoms were added to the structure models at calculated positions [ $d(C-H) = 0.95 \text{ \AA}$ ] and are unrefined [12]. The isotropic temperature factors for hydrogens were fixed to be 1.3 times the  $B_{eq}$  of the parent atom. The correct crystallographic enantiomer in the polar space group for **4** was determined by refinement of the positional parameters for both enantiomers and selection of the set of coordinates giving the better residuals. All calculations were carried out with the MolEN package [13] (definition of residuals:  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ,  $R_w = [\sum w ||F_o| - |F_c||^2 / \sum w |F_o|^2]^{1/2}$ ,  $GOF = [\sum w ||F_o| - |F_c||^2 / (n_o - n_p)]^{1/2}$  with  $n_o$  the number of structure factors and  $n_p$  the number of parameters,  $w = 1 / [\sigma(F_o)]^2$ ). Atomic coordinates and equivalent isotropic thermal parameters for **4** and **5** are listed in Tables 2 and 3 respectively. Further details of the crystal structure investigation may be obtained from the Fachinformationzentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany on quoting the depository number CSD-59316, the names of the authors and the journal citation.

### 3. Results and discussion

Ligand **4** was synthesized as depicted in Scheme 1. Williamson coupling of *o*-nitrophenol with dichloromethane, reduction of the nitro groups and subsequent formylation of the primary amines gave **3** which was converted into the diisocyanide by the phosgene method of Ugi and Meyr [14]. The ligand is a colorless crystalline solid which is soluble in all common organic solvents.

The IR spectrum shows the  $N \equiv C$  stretching absorption at  $\nu = 2127 \text{ cm}^{-1}$ . This value is in good agreement with those observed for other *o*-alkoxy substituted phenylisocyanides ( $2123 \text{ cm}^{-1}$  for **C**,  $2126 \text{ cm}^{-1}$  for **D** [6]). The resonance for the isocyanide carbon atom was observed as a broad singlet at  $\delta = 169.16 \text{ ppm}$  in the

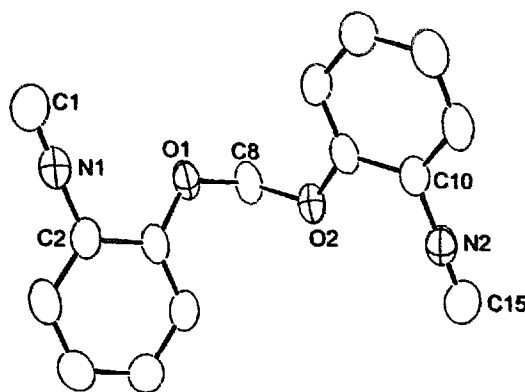


Fig. 2. ORTEP drawing of **4** showing 50% probability thermal ellipsoids.

$^{13}\text{C}$  NMR spectrum. In contrast to aliphatic isocyanides [4,15], only weak  $^1J(^{13}\text{C}^{14}\text{N})$  coupling was observed.

The molecular structure of **4** was determined by X-ray diffraction and a plot of the molecule is presented in Fig. 2. The structure analysis was carried out to compare bond parameters before and after coordination of the ligand. The free ligand exhibits typical  $N \equiv C$  distances of 1.152(3) and 1.150(3) Å and almost linear isocyanide groups ( $177.9(2)^\circ$  and  $178.0(2)^\circ$ , Table 4).

Table 4  
Selected bond distances (Å) and angles ( $^\circ$ ) for **5** and **4**

	<b>5</b>	<b>4</b>
Cr-C1	1.956(2)	
Cr-C15	1.963(2)	
Cr-C16	1.866(2)	
Cr-C17	1.891(3)	
Cr-C18	1.872(2)	
Cr-C19	1.888(3)	
N1-C1	1.153(3)	1.152(3)
N1-C2	1.389(3)	1.389(3)
N2-C10	1.390(3)	1.384(3)
N2-C15	1.150(3)	1.150(3)
C1-Cr-C15	84.27(9)	
C1-Cr-C16	174.37(10)	
C1-Cr-C17	96.25(11)	
C1-Cr-C18	88.03(9)	
C1-Cr-C19	86.83(10)	
C15-Cr-C16	95.00(9)	
C15-Cr-C17	88.32(11)	
C15-Cr-C18	171.93(10)	
C15-Cr-C19	88.96(10)	
C16-Cr-C17	89.30(11)	
C16-Cr-C18	92.91(10)	
C16-Cr-C19	87.58(11)	
C17-Cr-C18	90.14(11)	
C17-Cr-C19	175.67(11)	
C18-Cr-C19	93.02(10)	
Cr-C1-N1	174.3(2)	
Cr-C15-N2	174.5(2)	
C1-N1-C2	159.4(2)	177.9(2)
C10-N2-C15	168.3(2)	178.0(2)
O2-C8-O1	106.0(2)	112.1(2)

Reaction of equimolar amounts of **4** with  $[M(\text{nor}(\text{CO})_4)]$  ( $M = \text{Cr}, \text{Mo}$ ) in dichloromethane leads to the complexes  $[\text{Cr}(\text{4}(\text{CO})_4)]$  **5** and  $[\text{Mo}(\text{4}(\text{CO})_4)]$  **6** in good yield. The complexes were obtained after recrystallization as pale yellow crystals. The IR spectra show local  $C_{2v}$  symmetry, indicating that chelate complexes had formed. The IR absorptions of the complexes are comparable with the values observed for complexes of the type  $[\text{Cr}(\text{Ar}-\text{NC})_2(\text{CO})_4]$  [8,16]. The  $^{13}\text{C}$  NMR spectra of **5** and **6** show that the resonances for the isocyanide carbon atom are shifted downfield by 15 and 5 ppm respectively relative to the free ligand. The difference in deshielding can be attributed to the differences in the paramagnetic contribution to the chemical shift of chromium and molybdenum and, to a lesser extent, reflects the difference in the Lewis acidity of the metallocarbonyl fragments used. Additional evidence for the formation of chelate complexes can be drawn from the mass spectra. They show for both complexes the presence of molecule ions  $[\text{M}(\text{4}(\text{CO})_4)]^+$ . No peaks for higher molecular weights (e.g. for dinuclear complexes) were observed.

To establish **5** and **6** undoubtedly as monomeric chelate complexes, crystallization experiments were carried out and X-ray quality crystals of **5** were obtained. The structure analysis confirmed the conclusions drawn from the spectroscopic experiments (Fig. 3). Ligand **4** in crystalline **5** is coordinated in a *cis* fashion to the  $\text{Cr}(\text{CO})_4$  fragment. No variation in the  $\text{N}\equiv\text{C}$  bond distances of **4** was observed upon coordination (Table 4). However, the bond angles in **5** indicate that (d  $\rightarrow$  p) $\pi$  backbonding occurs in the metal complex. The  $\text{C}-\text{N}\equiv\text{C}$  angles change from almost linear in **4** to  $159.4(2)^\circ$  and  $168.3(2)^\circ$  in **5**. The shift of the  $\text{N}\equiv\text{C}$  absorption to lower wavenumbers in the IR spectrum indicates that this change is induced not only by the strain of the

chelate ring but is also caused by backbonding from the metal center to the isocyanide carbon atom. This backbonding should normally cause a lengthening of the  $\text{N}\equiv\text{C}$  bond. However, almost 20 years ago it was reported that backbonding to isocyanides can be detected by IR and NMR spectroscopy, but does not cause changes in the  $\text{N}\equiv\text{C}$  bond length [17,18]. We have recently reported a triisocyanide which contains only one coordinated isocyanide function. The crystal structure shows identical  $\text{N}\equiv\text{C}$  bond lengths for coordinated and free isocyanide groups, while their spectroscopic properties differ significantly [19].

The strain in the chelate ring of **5** is indicated by the change in the  $\text{O1}-\text{C8}-\text{O2}$  angle upon coordination. This angle changes from  $112.1(2)^\circ$  in the free ligand to  $106.0(2)^\circ$  in complex **5**.

With complexes **5** and **6** we present two examples for metal complexes with chelating bidentate isocyanides. To date no smaller backbone between two coordinated aromatic isocyanides has been reported. From the molecular parameters we conclude that the number of backbone atoms cannot be reduced any further if a bidentate aromatic isocyanide is to coordinate in a chelating fashion.

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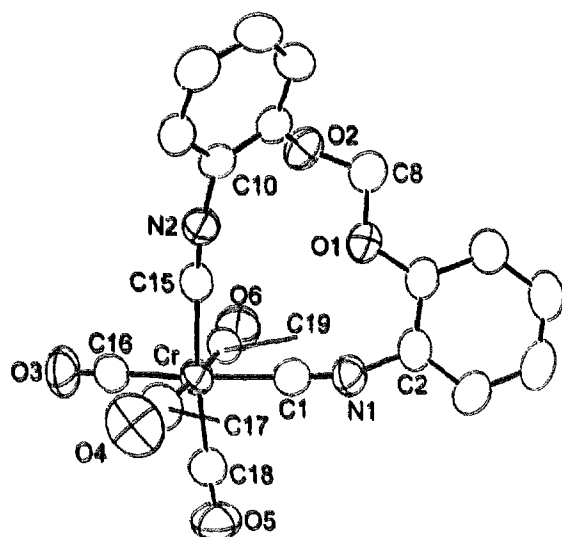


Fig. 3. ORTEP drawing of **5** showing 50% probability thermal ellipsoids.

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