

Note

# Synthesis of an anthracene-based bis(pyrazolyl)methane ligand and the structural characterization of its dinuclear tricarbonylrhenium(I) complex

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Received 1 February 2007; received in revised form 7 March 2007; accepted 7 March 2007

Available online 16 March 2007

## Abstract

The new anthracene-based, bitopic bis(pyrazolyl)methane ligand 1,8-bis(4-[bis(1-pyrazolyl)methyl]phenyl)anthracene (1,8-[4-CH(pz)<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>C<sub>14</sub>H<sub>8</sub>) has been prepared by the cobalt-catalyzed reaction between thionyl-dipyrzole and 1,8-bis(4-formylphenyl)anthracene. The reaction between 1,8-[4-CH(pz)<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>C<sub>14</sub>H<sub>8</sub> and Re(CO)<sub>5</sub>Br yielded the dirhenium complex {μ-1,8-[4-CH(pz)<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>C<sub>14</sub>H<sub>8</sub>}-[Re(CO)<sub>3</sub>Br]<sub>2</sub>. The solid state structure of this complex displays extensive noncovalent interactions, particularly CH–π and π–π interactions. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Bis(pyrazolyl)methane; Tricarbonylrhenium(I); Supramolecular; Anthracene

## 1. Introduction

The design of solid materials with useful properties relies on the thorough understanding of the factors that influence their molecular and supramolecular structures [1]. We have been exploring the coordination chemistry of poly(pyrazolyl)methane compounds that are functionalized at the carbon “backbone” to give “third-generation” poly(pyrazolyl)methane ligands [2,3]. Specifically, in these ligands two or more poly(pyrazolyl)methyl groups are linked through organic spacers to yield polytopic ligands. Using flexible [4], semi-rigid [5], and rigid [6] spacers, we have explored the roles that ligand size and flexibility play in dictating the final solid state structures of metal complexes. In addition, we have found that noncovalent interactions, such as π–π stacking and weak hydrogen bonds (CH–π and CH–X, where X = N, O, F) [7], made possible through the functionality built into the ligands, organize these complexes into supramolecular structures.

We previously reported the structures of multimetallic rhenium(I) complexes of the arene-linked ligands *m*-[CH(pz)<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>4</sub> [6a], *p*-[CH(pz)<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>4</sub> [6a], and 1,3,5-[CH(pz)<sub>2</sub>]<sub>3</sub>C<sub>6</sub>H<sub>3</sub> [6b]. Crystallographic studies revealed that CH–π and π–π interactions are dominant in directing the supramolecular structures of these complexes. To further explore the importance of such interactions among complexes comprising relatively rigid, arene-based ligands, we prepared the compound 1,8-bis(4-[bis(1-pyrazolyl)methyl]phenyl)anthracene (1,8-[4-CH(pz)<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>C<sub>14</sub>H<sub>8</sub>, **L**), an anthracene-based analogue to the phenylene- and mesitylene-linked ligands just described. The additional fused aryl groups of this ligand as well as its phenylene substituents increase the potential for both CH–π and π–π interactions. Herein, we describe the synthesis of **L** and the synthesis and structure of a dirhenium complex of this ligand.

## 2. Experimental section

### 2.1. General considerations

Air sensitive materials were handled under a nitrogen atmosphere using standard Schlenk techniques. All

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solvents were dried and distilled by conventional methods prior to use. The compounds  $\text{Re}(\text{CO})_5\text{Br}$  [8] and 1,8-bis(4-formylphenyl)anthracene [9] were prepared as previously described. All other chemicals were purchased from Aldrich or Fisher Scientific and used as received. Reported melting points are uncorrected. IR spectra were obtained on a Nicolet 5DXBO FTIR spectrometer. NMR spectra were recorded on a Mercury/VX 300 or Mercury/VX 400 spectrometer. All chemical shifts are in ppm and are secondary-referenced using the solvent signals. Mass spectrometric measurements were obtained on a VG 70S instrument or a Micromass Q-ToF spectrometer.

## 2.2. Syntheses

### 2.2.1. 1,8-Bis(4-[bis(1-pyrazolyl)methyl]phenyl)anthracene, 1,8-[4-CH(pz)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>C<sub>14</sub>H<sub>8</sub> (**L**)

Sodium hydride (1.20 g, 46.7 mmol) was suspended in 150 mL of THF and cooled in an ice-water bath for 30 min. Pyrazole (3.17 g, 46.6 mmol) was added, and the resulting solution was stirred at 0 °C for 30 min. Thionyl chloride (1.7 mL, 23.3 mmol) was added dropwise at 0 °C, and the resulting pale yellow suspension was allowed to reach room temperature while stirring for 40 min. Solid 1,8-bis(4-formylphenyl)anthracene (1.50 g, 3.88 mmol) and anhydrous  $\text{CoCl}_2$  (0.10 g, 0.77 mmol) were added to this suspension at once, and the system was heated at reflux for 24 h. After cooling to room temperature, water (50 mL) was added, and the system was stirred for 40 min. The resulting solution was extracted with  $\text{CH}_2\text{Cl}_2$  (1 × 50 mL, 2 × 20 mL) and the combined extracts washed with dilute aqueous NaCl and dried over  $\text{MgSO}_4$ . This mixture was filtered, the solvent removed by evaporation, and the solid taken up in  $\text{CH}_2\text{Cl}_2$  for chromatography ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  3/1). Yield = 0.74 g (31%). Mp: 252–254 °C. IR (KBr,  $\text{cm}^{-1}$ ): 3044, 2958, 1516, 1430, 1385, 739. <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.53 (s, 1H, 9- or 10-H anthracene), 8.39 (s, 1H, 9- or 10-H anthracene), 8.10 (s, 2H,  $\text{CH}(\text{pz})_2$ ), 8.04 (d,  $J = 8.0$  Hz, 2H, 4,5- or 2,7-H anthracene), 7.77 (d,  $J = 2.0$  Hz, 4H, 5-H pz), 7.69 (d,  $J = 2.0$  Hz, 4H, 3-H pz), 7.52 (dd,  $J = 8.6, 6.8$  Hz, 2H, 3,6-anthracene), 7.45 (d,  $J = 8.0$  Hz, 4H, 2,6- or 3,5- $\text{C}_6\text{H}_4$ ), 7.39 (d,  $J = 6.8$  Hz, 2H, 4,5- or 2,7-H anthracene), 7.06 (d,  $J = 8.0$  Hz, 4H, 2,6- or 3,5- $\text{C}_6\text{H}_4$ ), 6.42 (t,  $J = 2.0$  Hz, 4H, 4-H pz). <sup>13</sup>C NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  141.5, 141.2, 139.8, 135.7, 132.0, 130.7, 130.4, 130.2, 129.7, 128.2, 127.6, 127.0, 126.3, 125.6, 123.8, 107.0. HRMS: calcd. for  $\text{C}_{40}\text{H}_{30}\text{N}_8$  622.2593, found 622.2597. Direct probe MS  $m/z$  (rel. int.%) [assign]: 622 (40)  $[\text{M}]^+$ , 554 (40)  $[\text{M}-\text{Hpz}]^+$ , 486 (100)  $[\text{M}-2\text{Hpz}]^+$ .

### 2.2.2. $\{\mu\text{-}1,8\text{-}[4\text{-CH}(\text{pz})_2\text{C}_6\text{H}_4]_2\text{C}_{14}\text{H}_8\}\text{[Re}(\text{CO})_3\text{Br}]_2$ (**1**)

$\text{Re}(\text{CO})_5\text{Br}$  (0.33 g, 0.81 mmol) and 1,8-[4-CH(pz)<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>C<sub>14</sub>H<sub>8</sub> (**L**: 0.20 g, 0.32 mmol) were dissolved in 200 mL of acetone, and the solution was heated at reflux. After 2 d, a yellow precipitate had formed. After a total of 3 d at reflux, the system was cooled to room temperature.

The yellow solid was isolated by cannula filtration, washed with 5 mL of  $\text{Et}_2\text{O}$ , and dried *in vacuo*. Yield = 0.26 g (61%). Mp: 280 °C dec. IR,  $\nu_{\text{C}=\text{O}}$  (KBr,  $\text{cm}^{-1}$ ): 2026, 1908. <sup>1</sup>H NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  8.74 (s, 1H, 9- or 10-H anthracene), 8.67 (s, 2H,  $\text{CH}(\text{pz})_2$ ), 8.65 (d,  $J = 1.8$  Hz, 4H, 5-H pz), 8.62 (s, 1H, 9- or 10-H anthracene), 8.25 (d,  $J = 1.5$  Hz, 4H, 3-H pz), 8.12 (d,  $J = 6.3$  Hz, 2H, 4,5- or 2,7-H anthracene), 7.67 (d,  $J = 6.3$  Hz, 4H, 2,6- $\text{C}_6\text{H}_4$ ), 7.55 (dd,  $J = 5.1, 6.3$  Hz, 2H, 3,6-anthracene), 7.23 (d,  $J = 5.1$  Hz, 2H, 4,5- or 2,7-H anthracene), 6.97 (t,  $J = 1.8$  Hz, 4H, 4-H pz), 6.24 (d,  $J = 6.0$  Hz, 4H, 3,5- $\text{C}_6\text{H}_4$ ). Direct Probe MS  $m/z$  (rel. int.%) [assign]: 1322 (1)  $[\text{M}]^+$ , 1215 (4)  $[\text{M}-\text{Br}-\text{CO}]^+$ , 972 (10)  $[\text{M}-\text{Re}(\text{CO})_3\text{Br}]^+$ , 904 (5)  $[\text{M}-\text{Re}(\text{CO})_3\text{Br}-\text{Hpz}]^+$ , 820 (5)  $[\text{M}-\text{Re}(\text{CO})_3\text{BrH}-\text{pz}-3\text{CO}]^+$ , 622 (30)  $[\text{L}]^+$ , 554 (100)  $[\text{L}-\text{Hpz}]^+$ . HRMS ESI (+) for  $\text{M}-\text{Br}^-$   $[\text{C}_{46}\text{H}_{30}\text{BrN}_8\text{O}_6\text{Re}_2]^+$ : calcd. = 1243.0566; obs. = 1243.0558.

## 2.3. Crystal structure determination

X-ray intensity data from a colorless needle of **1** were measured at 150(1) K on a Bruker SMART APEX CCD-based diffractometer (Mo  $\text{K}\alpha$  radiation,  $\lambda = 0.71073$  Å) [10]. Raw data frame integration and Lp corrections were performed with SAINT+ [10]. Final unit cell parameters were determined by least-squares refinement of 7082 reflections with  $I > 5\sigma(I)$  from the data set. Analysis of the data showed negligible crystal decay during collection. The data were corrected for absorption effects with SADABS [10]. Direct methods structure solution, difference Fourier calculations and full-matrix least-squares refinement against  $F^2$  were performed with SHELXTL [11].

The compound crystallizes in the space group  $P2_1/n$  as determined by the pattern of systematic absences in the intensity data. The asymmetric unit contains one Re complex and a region of disordered solvent (centered at the origin and equivalent points). Several disorder models were attempted for these species but none were successful. Therefore, the disordered solvent was treated with the Squeeze program in Platon [12]. Electron density from a volume of 1750.8 Å<sup>3</sup> (30.8% total unit cell volume) corresponding to 411 e<sup>-</sup>/cell was removed from subsequent structure factor calculations by the program. The final tabulated  $F(000)$ , calculated density, and formula weight reflect known unit cell contents only. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as riding atoms (Table 1).

## 3. Results and discussion

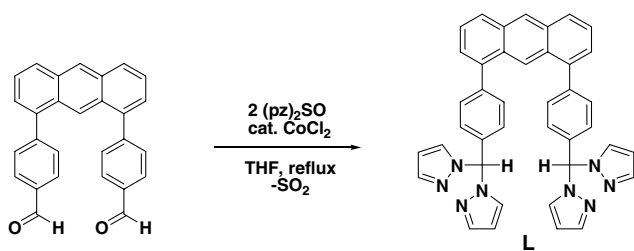
### 3.1. Syntheses

The new anthracene-based ligand 1,8-[4-CH(pz)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>-C<sub>14</sub>H<sub>8</sub> (**L**) was synthesized by the cobalt-catalyzed condensation reaction [13] between thionyl dipyrazole,  $\text{SO}(\text{pz})_2$ , prepared *in situ*, and the respective, previously reported

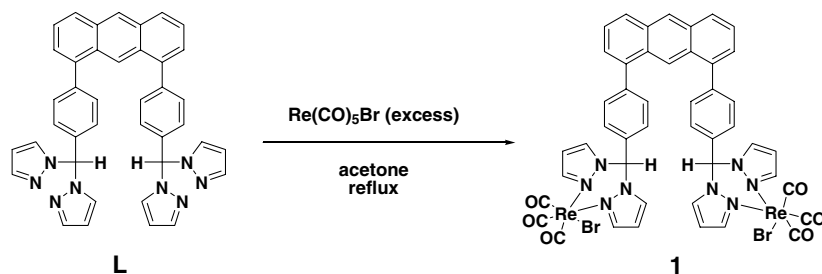
Table 1  
Crystal data and refinement details for  $\{\mu\text{-}1,8\text{-}[4\text{-CH}(\text{pz})_2\text{C}_6\text{H}_4]_2\text{C}_{14}\text{H}_8\}\text{-}[\text{Re}(\text{CO})_3\text{Br}]_2$  (**1**)

Empirical formula	$\text{C}_{46}\text{H}_{30}\text{Br}_2\text{N}_8\text{O}_6\text{Re}_2$
Formula weight	1323.00
Temperature (K)	150(1)
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
$a$ (Å)	13.6810(7)
$b$ (Å)	14.8887(8)
$c$ (Å)	28.1120(15)
$\alpha$ (°)	90
$\beta$ (°)	97.1940(10)
$\gamma$ (°)	90
$V$ (Å <sup>3</sup> )	5681.1(5)
$Z$	4
$D_{\text{calc}}$ (Mg m <sup>-3</sup> )	1.547
Absorption coefficient (mm <sup>-1</sup> )	5.710
Absorption correction	Semi-empirical from equivalents
$F(000)$	2520
Crystal size (mm <sup>3</sup> )	$0.26 \times 0.16 \times 0.06$
Theta range for data collection (°)	1.46–25.06
Index ranges	$-16 \leq h \leq 16, -17 \leq k \leq 17, -33 \leq l \leq 33$
$\lambda$ , Mo K $\alpha$ (Å)	0.71073
Reflections collected	53,835
Independent reflections [ $R_{\text{int}}$ ]	10,051 [0.0512]
Completeness to $\theta = 25.06^\circ$	99.8%
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0376; wR_2 = 0.0890$
Goodness-of-fit on $F^2$	1.057

dialdehyde [9] (Scheme 1). The ligand is a pale yellow solid freely soluble in halogenated solvents and in tetrahydrofuran. The reaction of **L** with  $\text{Re}(\text{CO})_5\text{Br}$  in refluxing acetone resulted in the precipitation of the yellow solid  $\{\mu\text{-}1,8\text{-}[4\text{-}$



Scheme 1. Preparation of 1,8-bis(4-[bis(1-pyrazolyl)methyl]phenyl)anthracene (**L**).



Scheme 2. Preparation of  $\{\mu\text{-}1,8\text{-}[4\text{-CH}(\text{pz})_2\text{C}_6\text{H}_4]_2\text{C}_{14}\text{H}_8\}\text{[Re}(\text{CO})_3\text{Br}]_2$  (**1**).

$\text{CH}(\text{pz})_2\text{C}_6\text{H}_4]_2\text{C}_{14}\text{H}_8\}\text{[Re}(\text{CO})_3\text{Br}]_2$  (**1**) within 2 d (Scheme 2). The complex is virtually insoluble in most common organic solvents except dimethyl sulfoxide (DMSO), in which it is freely soluble. Mass spectra of **1** show the parent ion and ions related to the loss of the  $[\text{Re}(\text{CO})_3\text{Br}]$  fragment as well as decomposition of the ligand, **L**. Infrared absorption bands indicate facial coordination of the carbonyl groups consistent with related compounds previously studied [6a,6b].

### 3.2. Solid state structure of **1**

Complex **1** was crystallized by the vapor diffusion of diethyl ether into DMSO solutions of the solid. ORTEP drawings showing two views of the complex are shown in Fig. 1, and selected bond distances and angles are given in Table 2. The two phenylene rings substituted onto the anthracene linker are rotated out of the plane of the linker, and the  $[\text{Re}(\text{CO})_3\text{Br}]$  moieties are also rotated away from each other, presumably reducing steric crowding in the molecule.

As observed in our previous studies of arene-linked, bis(pyrazolyl)methane complexes containing the  $[\text{Re}(\text{CO})_3\text{Br}]$  moiety [6a,6b], for **1** only one of the possible isomers about the rhenium is formed. NMR and IR characterization confirm the isomeric purity of the bulk products. The *trans*-effect is responsible for the observed facial arrangement of the CO ligands about rhenium, but of the two isomers of this type that may be formed upon coordination by the bis(pyrazolyl)methane donor, only one is observed for any of these complexes. This isomer, in which the bromine atom attached to rhenium is oriented *cis* to the methine proton in the boat or twist boat conformation of the six-membered metallocycle, allows a CO ligand on each rhenium to participate in an intramolecular  $\pi\text{-}\pi$  interactions with the proximate phenylene ring; the other isomer would place the bromine in this position. In compound **1** reported here, the distances from the phenylene ring centroids to the centers of the proximate C–O bond are 3.13 and 3.28 Å, and the perpendicular distances from the phenylene planes to the centers of the C–O bond are 3.11 and 3.20 Å. Since the perpendicular distances of strong  $\pi\text{-}\pi$  stacking interactions average 3.3–3.6 Å [14], the complexes presented here exhibit rather strong  $\pi\text{-}\pi$  interactions between the CO ligands and the linking phenylene ring.

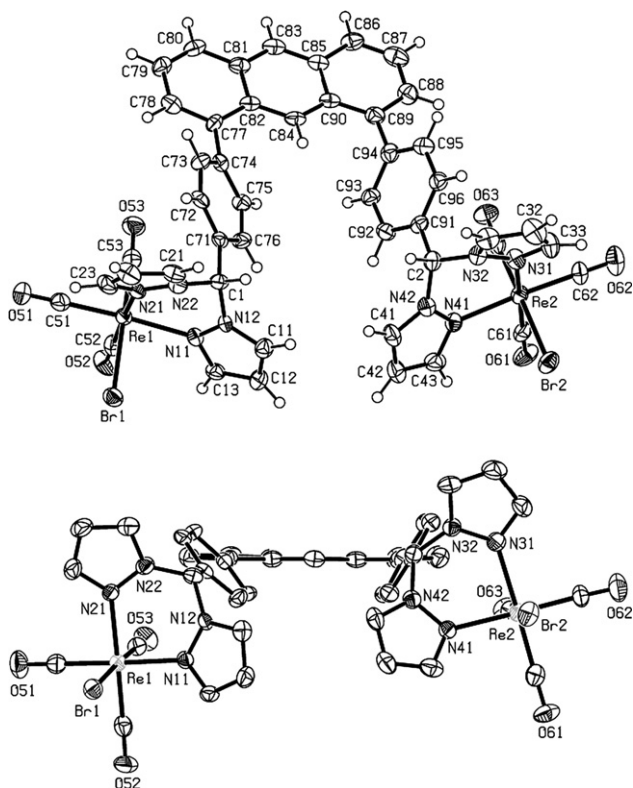


Fig. 1. ORTEP representations of  $\{\mu\text{-}1,8\text{-}[4\text{-CH}(\text{pz})_2\text{C}_6\text{H}_4]_2\text{C}_{14}\text{H}_8\}\text{-}[\text{Re}(\text{CO})_3\text{Br}]_2$  (**1**). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted from the bottom view.

We have proposed that weak intramolecular CH–Br interactions in the transition state of the reacting  $[\text{Re}(\text{CO})_3\text{Br}]$  unit and the ligands direct the formation of a single geometrical isomer analogous to those found in this work [15]. It is reasonable to assume that the same directing force is responsible for the formation of **1** and that additional stabilizing  $\pi\text{-}\pi$  interactions are also present between the CO ligands and the phenylene-linkers.

The molecules of **1** are organized into a three-dimensional supramolecular structure. CH– $\pi$  interactions produce the dimeric units shown in Fig. 2. The two molecules of each dimer exhibit two distinct, reciprocal CH– $\pi$  interactions between phenylene rings of one molecule (hydrogen atom donors: H(75) and H(93)) and the anthracene linker of the other molecule (hydrogen atom acceptors; H-centroid distances of 2.95 Å and 2.75 Å). Interestingly, although the planes containing the two anthracene linkers within the dimers are nearly parallel, the centroids of the arene rings within the anthracene linkers have “slipped” out of alignment such that no  $\pi\text{-}\pi$  stacking takes place. Instead, the phenylene substituents rotate out of the planes of the anthracene rings to be in position for the observed CH– $\pi$  interactions. Given the possibility for extensive  $\pi\text{-}\pi$  interactions, it is somewhat surprising that such stacking between anthracene units does not occur in **1**.

A combination of  $\pi\text{-}\pi$  and CH–X (X = Br, O) interactions, in addition to the CH– $\pi$  interactions creating the dimers just described, organize the three-dimensional

Table 2  
Selected bond distances (Å) and angles (°) for  $\{\mu\text{-}1,8\text{-}[4\text{-CH}(\text{pz})_2\text{C}_6\text{H}_4]_2\text{-C}_{14}\text{H}_8\}\text{-}[\text{Re}(\text{CO})_3\text{Br}]_2$  (**1**)

Re(1)–N(11)	2.183(5)
Re(1)–N(21)	2.185(5)
Re(1)–C(51)	1.916(7)
Re(1)–C(52)	1.909(7)
Re(1)–C(53)	1.924(7)
Re(1)–Br(1)	2.6502(6)
Re(2)–N(31)	2.186(5)
Re(2)–N(41)	2.171(5)
Re(2)–C(61)	1.904(7)
Re(2)–C(62)	1.919(6)
Re(2)–C(63)	1.903(6)
Re(2)–Br(2)	2.6231(6)
N(11)–Re(1)–N(21)	84.48(18)
N(11)–Re(1)–C(51)	174.7(2)
N(11)–Re(1)–C(52)	93.9(2)
C(51)–Re(1)–C(52)	88.6(2)
C(51)–Re(1)–C(53)	86.9(3)
C(51)–Re(1)–Br(1)	93.90(18)
N(31)–Re(2)–N(41)	84.85(18)
N(31)–Re(2)–C(61)	173.7(2)
N(31)–Re(2)–C(62)	93.8(2)
C(61)–Re(2)–C(62)	88.6(3)
C(61)–Re(2)–C(63)	91.4(2)
C(61)–Re(2)–Br(2)	90.43(18)

supramolecular structure for **1**. Helical chains that run along the *b*-axis are formed by a series of  $\pi\text{-}\pi$  stacking interactions, as shown in Fig. 3 (for clarity, the dimeric units are not shown). This  $\pi\text{-}\pi$  interaction exists between the N(21)- and N(31)-containing pyrazolyl rings on adjacent molecules along the helices (shortest perpendicular distance = 3.41 Å) and is the only  $\pi\text{-}\pi$  stacking present in the crystal structure. The helical chains are re-enforced by two CH–Br hydrogen bonds between Br(1) and the methine hydrogen atom H(2) (2.75 Å) and between Br(1) and the 5-pyrazolyl hydrogen atom H(41) (2.82 Å). Finally, a CH–O hydrogen bond (not pictured) between another 5-pyrazolyl hydrogen atom, H(21), and

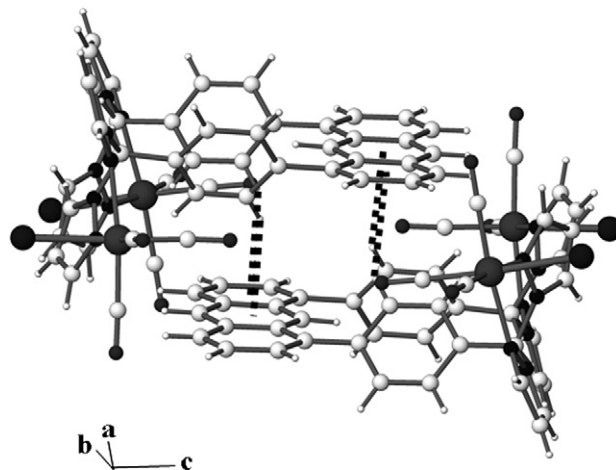


Fig. 2. Dimeric unit in **1** formed from reciprocal CH– $\pi$  interactions (dashed lines).



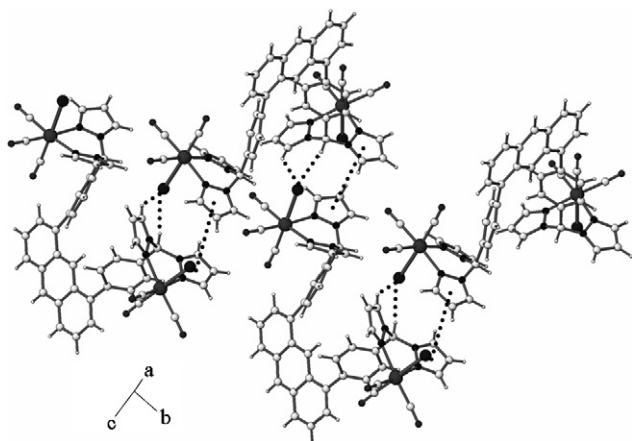


Fig. 3. Helical chains in **1** formed from  $\pi$ - $\pi$  interactions and CH-Br interactions (both sets shown as dashed lines).

O(61) of a carbonyl ligand links the helices into a three-dimensional structure.

### Acknowledgements

We thank the National Science Foundation (CHE-0414239) for financial support and Dr. Radu Semeniuc for helpful discussion. We also thank the Alfred P. Sloan Foundation for support of R.P.W. The Bruker CCD Single Crystal Diffractometer was purchased using funds provided by the NSF Instrumentation for Materials Research Program through Grant DMR: 9975623.

### Appendix A. Supplementary material

CCDC 632674 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.03.010](https://doi.org/10.1016/j.jorganchem.2007.03.010).

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