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μ-Furan-2,5-diylbis(methoxycarbene)-bis[pentacarbonylchromium(0)]

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.036
wR factor = 0.103
Data-to-parameter ratio = 14.4

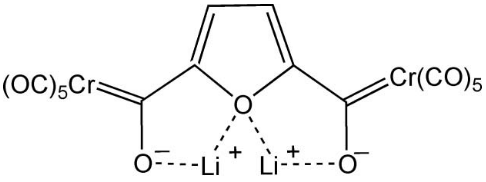
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The molecule of the title compound, [$Cr_2(C_8H_8O_3)(CO)_{10}$], comprises two octahedrally coordinated Cr atoms, each with five carbonyl ligands, and with a bis(methoxycarbene)furan ligand bridging the two Cr centres. The planar furan ring is coplanar with the two methoxycarbene groups. Structural data reveal some electron delocalization from one Cr atom to the other *via* the conjugated bridging bis-carbene ligand.

Comment

Innovators in materials science are devoting much attention to conjugated organometallic chain compounds for use in the fields of electronics, optics and ceramics (Long, 1995; Ward, 1995). Much of the research is directed at the study of the ‘push–pull’ effect in organometallic molecules, in which there is a charge redistribution across the molecule. High stabilities (Patil *et al.*, 1988) and large non-linear optical responses (Manna *et al.*, 1997) have been recorded for heteroaromatic groups in molecules with conjugated chain structures.

Although the synthetic utility of Fischer carbene complexes containing an unsaturated side chain has long been recognized, it is the physical properties, structural features (Sierra, 2000) and chemical properties (De Meijere *et al.*, 2000) of the compounds that provide impetus for research in this field. Dimetallic biscarbene complexes with heteroaromatic π-spacers have been prepared in our laboratories (Landman *et al.*, 2001*a*,*b*, 2002). This study focused not only on the synthesis and reactivities of such bis(carbene) complexes, but also on their electronic properties and structural features in solutions and in the solid state. The strongly electrophilic carbene C atom in Fischer carbene complexes is stabilized by a competitive π-donor interaction of the low oxidation state metal, the adjacent heteroatom and/or the unsaturated carbene substituent (Hofmann, 1983). If any of these π interactions is significant, one can expect an increase in bond order and restricted rotation around that particular bond.



(1)

The synthesis of Fischer-type bis(carbene) complexes involves three steps. In the first step, the furan is dilithiated (Chadwick & Willbe, 1977), followed, in the second step, by a

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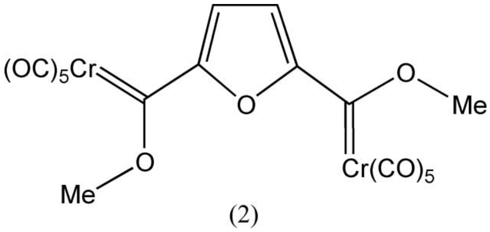
reaction at low temperature of the 2,5-dilithium furan with two equivalents of chromium hexacarbonyl (Fischer & Maasböl, 1964). This intermediate, (1), may influence the orientation of carbene substituents in the final product. If the intermediate displays interactions between the lithium cations and the O atoms of the acylate and furan groups, methylation (Christoffers & Dötz, 1994), in the third step, will be determined by the rigid structure resulting from the interactions of the ions. Hence, one would predict that the methoxy substituent would adopt a *cis* position about the C(carbene)—C(furan) bond with respect to the furan O atom, and, with little rotation around the C(carbene)—O bond, the methyl group should be *trans* to the furan ring. This is the structure observed for an analogous thiophene complex, *viz.* μ-thiophene-2,5-diylbis(ethoxycarbene)bis[pentacarbonylchromium(0)] (Terblans *et al.*, 1998). Bulky substituents will prefer less crowded positions and, with free rotation around the C(carbene)—C(furan) bond, the relative orientations may change. This was observed for the 3,6-dimethylthieno[3,2-*b*]thiophene unit in a bridging bis(carbene) complex, where both $Cr(CO)_5$ fragments were *trans* about the C(carbene)—C(thiophene) bonds with respect to the thiophene S atoms (Landman *et al.*, 2001*b*, 2002).



(2)

Although the structure of furan in the gas phase has been determined by microwave spectroscopy (Bak *et al.*, 1962; Mata *et al.*, 1978), the experimental results for the gas phase differed substantially from those reported for the crystalline phase (Fourme, 1972). The geometrical parameters obtained for furan, assuming planarity and C_{2v} symmetry and using several structural analyses employing various combinations of data from gas-phase electron diffraction, rotational spectroscopy and liquid crystal NMR spectroscopy, are O—C1/4 = 1.3641 (7) Å, C1/4—C2/3 = 1.3640 (9) Å and C2—C3 = 1.4303 (19) Å, and C1—O—C4 = 106.74 (7)° and O—C1/4—C2/3 = 110.49 (7)° (Liecheski & Rankin, 1989). Selected bond lengths and angles of the title bis(carbene) complex, (2), are tabulated in Table 1. The six ligands, five carbonyls and one carbene, are arranged octahedrally around each Cr centre. The Cr1—C(carbene) bond distance is significantly longer than the Cr2—C(carbene) distance. The thiophene bis(carbene) complex does not exhibit such a discrepancy between the two metal–carbene bonds [2.040 (5) *versus* 2.043 (5) Å]. This could be due to the orientation of the Cr–carbene fragments with respect to the heterocycle. Fig. 1 shows clearly that Cr1 is *trans* and Cr2 is *cis* about the respective C(carbene)—C(furan) bonds with respect to the furan O atom, while in the analogous thiophene compound the metal atoms are both *trans* about the C(carbene)—C(thiophene) bonds with respect to the thiophene S atom. To compensate for the differences in Cr—C(carbene) distances, the *trans* Cr—C(carbonyl) bonds in (2) are affected in such a way that the two C(carbonyl)—Cr—C(carbene) distances are the same within experimental error [C4···C15 = 3.930 (3) Å and C7···C25 = 3.919 (3) Å]. There is thus a greater degree of π back-bonding to the *trans* carbonyl on the Cr1 side, with shorter carbonyl but longer Cr–carbene distances, while the opposite, *i.e.* longer carbonyl but shorter Cr–carbene distances, is true on the Cr2 side. This implies that Cr1 is more negatively charged compared with Cr2 and is indicative of a 'push–pull' effect across the bridging ligand. The Cr—C(carbene) bond lengths are comparable with values of 2.0–2.1 Å found in the literature (Schubert, 1983) for chromium–alkoxy–carbene complexes, and the longer value [2.038 (2) Å] agrees excellently with the observed value of 2.040 (5) Å recorded for the analogous thiophene–dichromium–bis(carbene) complex.

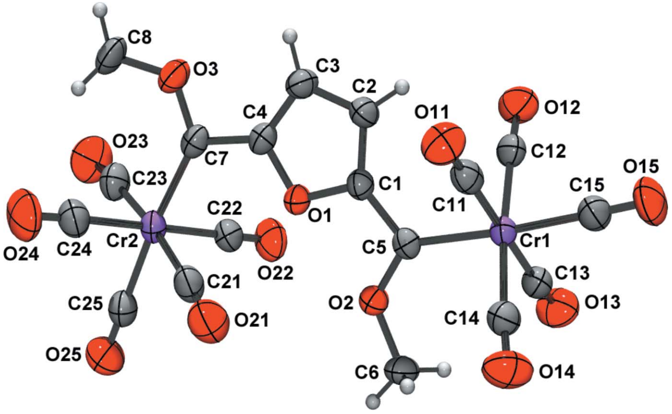
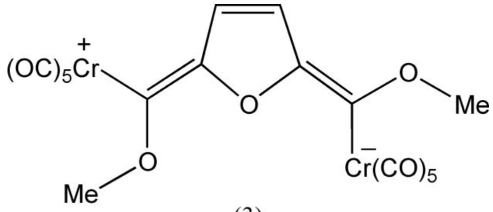


Figure 1
A view of the molecular structure of (2), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms drawn as spheres of arbitrary radius.

The coplanarity of the furan ring and carbene C and Cr atoms in the solid state favours electron delocalization. The furan ring is essentially planar: the greatest deviation from the mean plane through atoms O1, C1, C2, C3 and C4 is 0.005 (1) Å for O1. The carbene groups are also both close to being planar: the greatest deviations from the mean planes through atoms Cr1, O2, C1 and C5, and atoms Cr2, O3, C4 and C7, are 0.003 (2) Å for C5 and 0.008 (2) Å for C7, respectively. The carbene groups are also both close to being coplanar with the furan ring: the angles between the carbene mean planes and the furan mean plane are 3.2 (1) and 4.7 (1)°, respectively. The bond angles around the sp^2-carbene C atoms are not the ideal 120° values, but nevertheless are typical for alkoxy–carbene complexes (Goddard *et al.*, 1980). On comparing the bond lengths of the furan ring in the complex with the bond lengths of furan itself, evidence is found of electron delocalization through the heteroaromatic ring. All the C—C bonds are equal to within 0.03 Å, with the C2—C3 bond shorter and the C1—C2 and C3—C4 bonds longer than the mean. The delocalization is carried forward to the C(carbene)—C(furan) bond, which is also shorter than normal Csp^2—Csp^2 single bonds (Allen *et al.*, 1987). These structural features not only indicate efficient electron delocalization through the conjugated bridging ligand, but support some charge distribution corresponding to a 'push–pull' effect along the molecular long axis. This effect is illustrated by a resonance structure, (3), shown in the scheme below.



(3)

Experimental

The title compound was isolated as the main product from the reaction of dilithiated furan (Chadwick & Willbe, 1977) and two equivalents of hexacarbonylchromium (Crause *et al.*, 2005) and subsequent alkylation with six equivalents of methyl trifluoromethanesufonate (Christoffers & Dötz, 1994). The title compound was purified and isolated as a purple band from a silica-gel 60 column using a 2:1 mixture of hexane and dichloromethane as eluant. Recrystallization from dichloromethane and hexane gave dark-purple crystals suitable for X-ray diffraction studies.

Crystal data

$[Cr_2(C_8H_8O_3)(CO)_{10}]$
$M_r = 536.24$
Triclinic, $P\overline{1}$
$a = 6.3656$ (4) Å
$b = 13.5100$ (10) Å
$c = 13.9374$ (10) Å
$\alpha = 114.454$ (1)°
$\beta = 93.965$ (1)°
$\gamma = 100.785$ (1)°
$V = 1057.31$ (13) Å^3
$Z = 2$
$D_x = 1.684$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3938 reflections
$\theta = 2.8$–$26.2°$
$\mu = 1.10$ mm^{-1}
$T = 293$ (2) K
Plate, dark purple
0.38 × 0.24 × 0.04 mm

Data collection

Bruker *SMART* CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{min} = 0.798$, $T_{max} = 0.957$
6293 measured reflections
4304 independent reflections
3678 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 26.4°$
$h = -7 \rightarrow 4$
$k = -16 \rightarrow 16$
$l = -16 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.103$
$S = 1.04$
4304 reflections
298 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0574P)^2 + 0.3404P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cr1—C12	1.890 (2)	O1—C4	1.358 (2)
Cr1—C15	1.894 (2)	O1—C1	1.384 (2)
Cr1—C13	1.894 (2)	C1—C2	1.374 (3)
Cr1—C11	1.904 (2)	C1—C5	1.455 (3)
Cr1—C14	1.921 (2)	C2—C3	1.396 (3)
Cr1—C5	2.038 (2)	C3—C4	1.367 (3)
Cr2—C24	1.898 (2)	C4—C7	1.470 (3)
Cr2—C23	1.899 (3)	C5—O2	1.326 (2)
Cr2—C25	1.907 (3)	O2—C6	1.438 (3)
Cr2—C22	1.913 (2)	C7—O3	1.330 (3)
Cr2—C21	1.921 (3)	O3—C8	1.435 (3)
Cr2—C7	2.016 (2)		
C4—O1—C1	107.61 (15)	O2—C5—Cr1	131.04 (15)
C2—C1—O1	108.02 (18)	C1—C5—Cr1	122.72 (14)
C1—C2—C3	107.76 (19)	O3—C7—C4	103.18 (18)
C4—C3—C2	106.90 (19)	O3—C7—Cr2	132.66 (15)
O1—C4—C3	109.70 (18)	C4—C7—Cr2	124.14 (15)
O2—C5—C1	106.23 (16)		

All H atoms were located in difference maps, but were constrained in the refinement to ride on the C atoms to which they were bonded, with Csp^2—H = 0.93 Å and methyl C—H = 0.96 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *POV-RAY* (Cason, 2004); software used to prepare material for publication: *SHELXL97*.

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References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Bak, B., Christensen, D., Dixon, W. B., Hansen-Nygaard, L., Andersen, J. R. & Schottlander, M. (1962). *J. Mol. Spectrosc.* **9**, 124–129.
Bruker (2001). *SMART* (Version 5.054), *SAINT* (Version 6.45), *SADABS* (Version 2.10) and *SHELXTL* (Version 6.12). Bruker AXS Inc., Madison, Wisconsin, USA.
Cason, C. J. (2004). *POV-RAY for Windows*. Version 3.1. Persistence of Vision Raytracer Pty. Ltd., Victoria, Australia. URL: http://www.povray.org/
Chadwick, D. T. & Willbe, C. (1977). *J. Chem. Soc. Perkin Trans. 1*, pp. 887–892.
Christoffers, J. & Dötz, K.-H. (1994). *Organometallics*, **13**, 4189–4193.
Crause, C., Görls, H. & Lotz, S. (2005). *J. Chem. Soc. Dalton Trans.* pp. 1649–1657.
De Meijere, A., Schirmer, H. & Deutch, M. (2000). *Angew. Chem. Int. Ed.* **39**, 3964–4002.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Fischer, E. O. & Maasböl, A. (1964). *Angew. Chem. Int. Ed. Engl.* **3**, 580–581.
Fourme, R. (1972). *Acta Cryst.* B**28**, 2984–2991.
Goddard, R. J., Hoffmann, R. & Jemmis, E. M. (1980). *J. Am. Chem. Soc.* **102**, 7667–7676.
Hofmann, P. (1983). *Transition Metal Carbene Complexes*, pp. 113–149. Weinheim: Verlag Chemie.
Landman, M., Görls, H. & Lotz, S. (2001*a*). *J. Organomet. Chem.* **617–618**, 282–289.
Landman, M., Görls, H. & Lotz, S. (2001*b*). *Eur. J. Inorg. Chem.* pp. 233–238.

Landman, M., Görls, H. & Lotz, S. (2002). *Z. Anorg. Allg. Chem.* **628**, 2037–2043.

Liecheski, P. B. & Rankin, D. W. H. (1989). *J. Mol. Struct.* **196**, 1–19.

Long, N. J. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 21–38.

Manna, J., Kuehl, C. J., Whiteford, J. A. & Stang, P. (1997). *Organometallics*, **16**, 1897–1905.

Mata, F., Martin, M. C. & Sorensen, G. O. (1978). *J. Mol. Struct.* **48**, 157–163.

Patil, A. O., Heeger, A. J. & Wudl, F. (1988). *Chem. Rev.* **88**, 183–200.

Schubert, U. (1983). *Transition Metal Carbene Complexes*, pp. 73–111. Weinheim: Verlag Chemie.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Sierra, M. A. (2000). *Chem. Rev.* **100**, 3591–3637.

Terblans, Y. M., Roos, R. M. & Lotz, S. (1998). *J. Organomet. Chem.* **566**, 133–142.

Ward, M. D. (1995). *Chem. Soc. Rev.* **24**, 121–134.