The authors wish to acknowledge the purchase of the CAD-4 diffractometer under grant DPT/TBAG1 of The Scientific and Technical Research Council of Turkey.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: BM1026). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5. Enraf–Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Mak, T. C. W., Smith, G. & Kennard, C. H. L. (1993). *Z. Kristallogr.* **207**, 33–38.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Pescher, R. & Schenk, H. (1987). *Acta Cryst.* A**43**, 751–763.

Smith, G., Kennard, C. H. L. & Mak, T. C. W. (1988). *Z. Kristallogr.* **184**, 275–280.

Usubaliev, G. J., Movsumov, E. M., Amiraslanov, I. R., Akhmedor, A. I., Musaev, A. & Mamedov, Kh. S. (1981). *J. Struct. Chem.* **22**, 73–77.

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Tricarbonyl(η^6-3-methyl-2-vinylbenzoic acid)chromium

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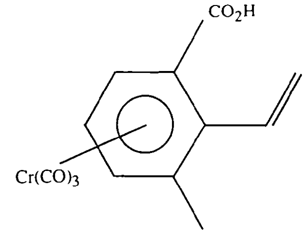
Abstract

The benzylic deprotonation of tricarbonyl(η^6-1-*tert*-butoxycarbonyl-2,3-dimethylbenzene)chromium occurs preferentially at the *ortho* position, whereas the *meta* position is still reactive but to a lesser extent. X-ray study of the title compound, $[Cr(CO)_3(C_{10}H_{10}O_2)]$, obtained in a very good yield, confirms this result and shows a strong hydrogen bond between neighbouring carboxy groups. The acid group and the phenyl ring are coplanar and the torsion angle between the phenyl ring and the vinyl group is 61.2°(4).

Comment

The chemistry and applications of tricarbonyl(η^6-arene)-chromium are of great interest (Uemura, 1991). The behaviour of stabilized benzylic anions generated by potassium *tert*-butoxide in the presence of aldehyde and by ^{n}BuLi in the presence of alkyl halide has been analysed (Jaouen, Top, Laconi, Couturier & Brocard, 1984; Blagg, Davies & Mobbs, 1985; Blagg & Davies, 1985). Electronic effects in directing the regioselectivity of benzylic attack were found (Brocard & Lebibi, 1987). In order to study the selectivity of proton abstraction from *ortho* and *meta* benzylic sites relative to an electron-withdrawing group, tricarbonyl(η^6-1-*tert*-butoxycarbonyl-2,3-dimethylbenzene)chromium was reacted at room temperature with potassium *tert*-butoxide in DMSO with aldehyde (H_2—C=O) and afforded the *ortho* ethylenic acid tricarbonyl(η^6-3-methyl-2-vinylbenzoic acid)chromium, (I), in 97% yield. The difference in reactivity opens up the possibility of controlled introduction of two different electrophiles (Brocard, Pelinski & Goetgheluck, 1994).



(I)

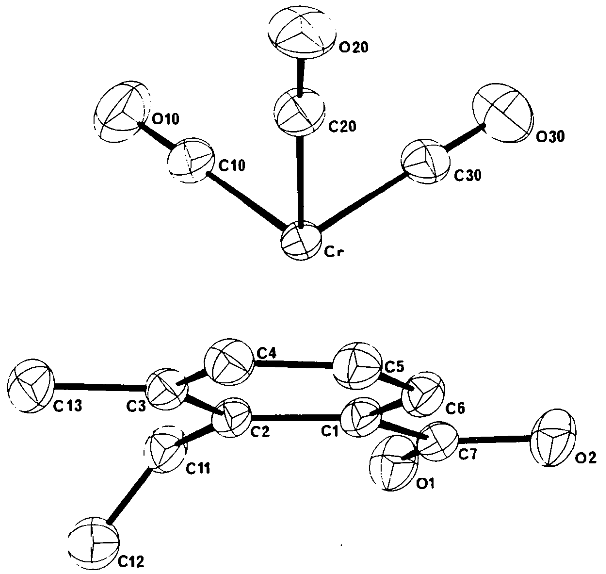


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the title compound showing the atom-labelling scheme with ellipsoids at the 50% probability level.

300 MHz ^{1}H NMR spectra indicated that the vinyl group is in an *ortho* position with respect to the acid group. The X-ray crystallographic study confirms the regioselectivity of deprotonation. Fig. 1 shows the conformation of the molecule. The acid group (C7—O1—O2—H) and the phenyl ring are coplanar: torsion angle C2—C1—C7—O1 = 0.3°(3). The vinyl group lies out of this plane on the opposite side of the plane with respect to the tricarbonylchromium group: torsion angle C3—C2—C11—C12 = 61.2°(4). There is an intermolecular hydrogen bond between neighbouring carboxy groups related by the symmetry operation $-x-1$, $-y$, $-z$.

Experimental

Spectroscopic data for the title compound are as follows. 300 MHz ^{1}H NMR: δ 6.82 (1*H*, *dd*, *J* 17.6 and 11.2 Hz, CH=CH$_2$), 6.01 (1*H*, *d*, *J* 6.1 Hz, C$_6$H$_3$), 5.62 (1*H*, *d*, *J* 11.2 Hz, CH=CH$_2$), 5.52 (1*H*, *d*, *J* 6.1 Hz, C$_6$H$_3$), 5.35 (1*H*, *d*, *J* 17.6 Hz, CH=CH$_2$), 5.30 (1*H*, *t*, *J* 6.2 Hz, C$_6$H$_3$), 2.21 p.p.m. (3*H*, *s*, CH$_3$ *meta*). MS: *m/z* (%) 298 (M^+, 8), 242 (M^+ −2CO, 1), 214 (M^+ −3CO, 90), 162 [M^+ −Cr(CO)$_3$, 26], 52 (Cr$^+$, 100). The crystals were obtained by slow cooling (263 K) of a solution in 2-propanol.

Crystal data

$[Cr(CO)_3(C_{10}H_{10}O_2)]$
$M_r = 298.2$
Triclinic
$P\bar{1}$
$a = 6.966\,(4)$ Å
$b = 8.993\,(4)$ Å
$c = 10.932\,(4)$ Å
$\alpha = 96.03\,(15)°$
$\beta = 104.12\,(16)°$
$\gamma = 104.84\,(16)°$
$V = 632\,(4)$ Å^3
$Z = 2$
$D_x = 1.57$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 20–27°$
$\mu = 0.918$ mm^{-1}
$T = 293$ K
Parallelepiped
0.5 × 0.5 × 0.4 mm
Yellow

Data collection

Philips PW1100 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4992 measured reflections
4728 independent reflections
2094 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.03$
$\theta_{\rm max} = 37°$
$h = -8 \rightarrow 8$
$k = -11 \rightarrow 11$
$l = 0 \rightarrow 20$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F
$R = 0.0474$
$wR = 0.0479$
$S = 1.15$
2094 reflections
175 parameters
$w = 1/[\sigma^2(F_o) + 0.0011F_o^2]$
$(\Delta/\sigma)_{\rm max} = 0.03$

$\Delta\rho_{\rm max} = 0.37$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.31$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV), and Stewart, Davidson & Simpson (1965) for H atoms

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cr	0.2091 (1)	0.3759 (1)	0.2341 (1)	0.035 (1)
C10	−0.0043 (6)	0.4622 (4)	0.1831 (4)	0.060 (5)
O10	−0.1391 (5)	0.5141 (4)	0.1508 (4)	0.106 (5)
C20	0.3914 (6)	0.5759 (4)	0.2625 (4)	0.060 (5)
O20	0.4991 (6)	0.6987 (4)	0.2770 (4)	0.084 (5)
C30	0.1933 (7)	0.4080 (5)	0.4003 (4)	0.061 (5)
O30	0.1830 (6)	0.4256 (4)	0.5042 (3)	0.110 (6)
C1	0.0225 (5)	0.1492 (4)	0.1190 (3)	0.042 (4)
C2	0.1382 (5)	0.1200 (4)	0.2360 (3)	0.042 (3)
C3	0.3577 (6)	0.1860 (4)	0.2757 (4)	0.048 (4)
C4	0.4539 (6)	0.2767 (5)	0.1990 (4)	0.058 (5)
C5	0.3410 (6)	0.3010 (5)	0.0807 (4)	0.065 (5)
C6	0.1260 (6)	0.2364 (4)	0.0402 (4)	0.053 (4)
C7	−0.2076 (5)	0.0894 (4)	0.0723 (3)	0.043 (4)
O1	−0.3125 (4)	0.0118 (3)	0.1317 (3)	0.063 (3)
O2	−0.2868 (4)	0.1262 (3)	−0.0373 (3)	0.060 (3)
C11	0.0336 (6)	0.0198 (5)	0.3159 (4)	0.053 (4)
C12	0.0735 (7)	−0.1113 (5)	0.3388 (5)	0.074 (6)
C13	0.4923 (6)	0.1630 (5)	0.3986 (4)	0.062 (5)

Table 2. *Selected geometric parameters (Å, °)*

Cr—C10	1.844 (4)	C1—C2	1.425 (5)
Cr—C20	1.861 (4)	C1—C6	1.426 (5)
Cr—C30	1.845 (4)	C1—C7	1.490 (5)
Cr—C1	2.176 (4)	C7—O1	1.228 (5)
Cr—C2	2.230 (4)	C7—O2	1.306 (4)
Cr—C3	2.244 (4)	C2—C3	1.427 (6)
Cr—C4	2.208 (5)	C2—C11	1.498 (6)
Cr—C5	2.222 (4)	C11—C12	1.313 (6)
Cr—C6	2.207 (4)	C3—C4	1.398 (6)
C10—O10	1.149 (6)	C3—C13	1.507 (6)
C20—O20	1.135 (5)	C4—C5	1.411 (6)
C30—O30	1.153 (5)	C5—C6	1.398 (6)
C1—Cr—C2	37.7 (1)	C2—C11—C12	121.9 (4)
C1—Cr—C6	38.0 (1)	C2—C3—C4	119.5 (4)
C2—Cr—C3	37.2 (1)	C2—C3—C13	122.6 (4)
C3—Cr—C4	36.6 (2)	C4—C3—C13	118.2 (4)
C4—Cr—C5	37.1 (2)	C3—C4—C5	121.9 (4)
C5—Cr—C6	36.8 (2)	C4—C5—C6	119.3 (4)
C10—Cr—C20	87.8 (2)	C5—C6—C1	120.1 (4)
C20—Cr—C30	90.1 (2)	C6—C1—C2	120.3 (3)
C10—Cr—C30	89.7 (2)	C6—C1—C7	117.2 (3)
C1—C2—C3	118.8 (3)	C2—C1—C7	122.5 (3)
C1—C2—C11	121.1 (3)	C1—C7—O1	122.8 (3)
C3—C2—C11	120.0 (3)	C1—C7—O2	114.0 (3)
C2—C1—C7—O1	0.3 (3)	C3—C2—C11—C12	−61.2 (4)

D—H···A	H···A	D···A	D—H···A
O2—H2···O1$^{\rm i}$	1.867 (5)	2.639 (4)	170 (4)

Symmetry code: (i) $-1-x$, $-y$, $-z$.

All H atoms were located from a difference Fourier synthesis, then replaced in theoretical positions. Only the coordinates of the H2 atom, involved in the hydrogen bond, were refined. All calculations were performed on a MicroVAX II computer.

Data collection: Philips PW1100 software. Cell refinement: Philips PW1100 software. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86

(Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP* (Johnson, 1976); *PLUTO* (Motherwell & Clegg, 1978) .

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1203). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Blagg, J., Davies, S. & Mobbs, B. (1985). *J. Chem. Soc. Chem. Commun.* p. 619.

Blagg, J. & Davies, S. (1985). *J. Chem. Soc. Chem. Commun.* p. 653.

Brocard, J. & Lebibi, J. (1987). *J. Organomet. Chem.* **320**, 295–306.

Brocard, J., Pelinski, L. & Goetgheluck, S. (1994). *J. Organomet. Chem.* **476**, C12–C14.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf–Nonius, Delft, The Netherlands.

Jaouen, G., Top, S., Laconi, A., Couturier, D. & Brocard, J. (1984). *J. Am. Chem. Soc.* **106**, 2207–2208.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures.* University of Cambridge, England.

Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* University of Cambridge, England.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* Univiversity of Göttingen, Germany.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Uemura, M. (1991). *Adv. Org. Chem.* **2**, 195–245

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Bis(cyclooctatetraenyl)neptunium(IV)

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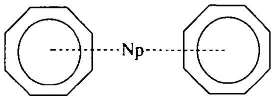
Abstract

The crystal structure of neptunocene, $[\mathrm{Np(C_8H_8)_2}]$, has been determined by single-crystal X-ray diffraction and is isostructural with thorocene and uranocene. A number of crystallographic and geometric parameters of these three compounds are compared.

Comment

The crystal and molecular structures of the two isostructural cyclooctatetraene dianion π-complexes thorocene and uranocene, $[\mathrm{Th(C_8H_8)_2}]$ and $[\mathrm{U(C_8H_8)_2}]$, have been described by Avdeef, Raymond, Hodgson & Zalkin (1972). Karraker, Stone, Jones & Edelstein (1970) obtained X-ray powder diffractograms of uranocene and of the neptunium (neptunocene) and plutonium (plutonocene) analogues showing evidence that all three actinide(IV)–cyclooctatetraenes are isomorphous. Two groups, Goffart, Fuger, Brown & Duyckaerts (1974), and Starks, Parsons, Streitwieser & Edelstein (1974), have, independently from each other and almost simultaneously, shown that the protactinium analogue is isostructural with the lower actinides mentioned above. In the present paper the molecular and crystal structure of neptunocene, (I), is described and its geometry with respect to thorocene and uranocene discussed.



(I)

The molecular structure of the title compound, (I), consists of a central Np atom symmetrically π-bonded to two aromatic cyclooctatetraene dianion rings related by a crystallographic inversion centre. Neptunocene has D_{8h} symmetry: the molecular eightfold axis passes through the centre of the two rings and the Np atom (Fig. 1).

The cyclooctatetraene dianion rings are planar within the limits of accuracy, the maximum deviation of a ring atom through the least-squares plane being 0.014 (8) Å (C3). The planarity of the ring and the mean bond lengths [1.385 (5) Å] and angles [135.0 (3)°] demonstrate the aromatic nature of the 10-π-electron dianion rings in (I). The aromaticity is also confirmed by a comparison of the two averages for alternate sets of four C—C bonds. Such a comparison is a much more severe test for the aromaticity of the anion than bond-by-bond comparisons of the overall average since the averages must be equal in an aromatic hydrocarbon ring. In the title compound the averages, 1.388 (7) and 1.383 (7) Å, are equal to within one e.s.d.

In the crystal, the molecules alternate in a herringbone motif up the twofold screw axis, parallel to *b* (Fig. 2). The same motif has been found in the thorium and uranium analogues (Avdeef, Raymond, Hodgson & Zalkin, 1972).

The molecular structure corroborates the Mössbauer studies of Karraker, Stone, Jones & Edelstein (1970), which indicated 'the presence of at least some π-interaction between the ligand molecular orbitals and metal 5*f* orbitals', and by Adrian, Appel, Bohlander, Haffner, Kanellakopulos & Krüger (1986).

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