*Acta Cryst.* (1992). C48, 636–638

# Structure of Tricarbonyl[(1,2,3,4,5,6-$\eta$)-*N*,*N*-diethyl-2-methoxy-4,5-dimethylbenzamide]chromium(0)

By George R. Clark,* Kee Chee Lee and Paul D. Woodgate

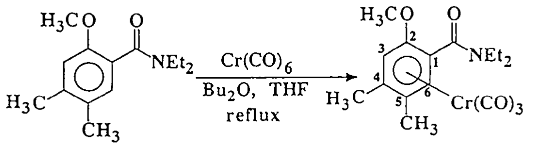
*Department of Chemistry, University of Auckland, Auckland, New Zealand*

(*Received* 5 *April* 1991; *accepted* 12 *September* 1991)

**Abstract.** $[Cr(CO)_3(C_{14}H_{21}NO_2)]$, $M_r = 371.36$, triclinic, $P\bar{1}$, $a = 11.131$ (1), $b = 12.708$ (1), $c = 6.902$ (1) Å, $\alpha = 97.58$ (1), $\beta = 103.39$ (1), $\gamma = 67.38$ (1)°, $V = 875.7$ (2) Å$^3$, $Z = 2$, $D_x = 1.408$ g cm$^{-3}$, Cu $K\alpha$, $\lambda = 1.5418$ Å, $\mu = 89.8$ cm$^{-1}$, $F(000) = 388$, $T = 292 \pm 1$ K, final $R = 0.037$ for 2738 reflections. The complex exhibits the 'piano-stool' structure typical of ($\eta^6$-arene)$Cr(CO)_3$ compounds. The $Cr(CO)_3$ tripod is eclipsing towards C(2), C(4) and C(6), leaving the amide moiety free to adopt an almost perpendicular orientation with respect to the arene ring.

**Introduction.** The title compound was prepared during experiments designed to study the reactivity of an aromatic ring complexed to chromium(0) (Cambie, Erson, Gourdie, Rutledge & Woodgate, 1988). In view of the fact that the NMR spectra were ambiguous in some aspects of the signal assignments, we have carried out a single-crystal X-ray structure determination in order to verify the structure of the complex, and to determine the conformation of the three carbonyl ligands with respect to the aromatic ring.

**Experimental.** Hexacarbonylchromium(0) was refluxed in a light-protected flask with *N*,*N*-diethyl-2-methoxy-4,5-dimethylbenzamide in dibutyl ether/THF (12:1) for 5 h. The mixture was allowed to cool to room temperature and then concentrated *in vacuo* to give a mixture of starting material and its tricarbonylchromium(0) complex.



The stable complex ($C_{17}H_{21}CrNO_5$, m.p. 441–443 K, 24%) was separated easily from starting material since the latter was soluble in dichloromethane whereas the complex was not. In the infrared spectrum, three strong peaks ($\nu_{max}$ 1950, 1882 and 1858 cm$^{-1}$) were indicative of the three carbonyl ligands. A characteristic feature of the $^1$H NMR spectra of these complexes is the upfield shift of signals due to arene protons [H(3) $\delta_H$ 4.96, H(6) $\delta_H$ 5.69]. Assignment of these protons was confirmed by analysis of the long-range COSY spectrum; since the singlet at $\delta_H$ 3.79 due to $OCH_3$ showed coupling ($^5J$) to H(3) [but not to H(6)], the singlet at $\delta_H$ 4.96 was confirmed as being due to H(3). Similarly, 4-$CH_3$ ($\delta_H$ 2.28) was differentiated from 5-$CH_3$ ($\delta_H$ 2.09) in the COSY spectrum, in which the 4-$CH_3$ correlated ($^4J$) to H(3) while 5-$CH_3$ correlated ($^4J$) to H(6). The methyl and the methylene protons in the diethylamido side chain were assigned by comparison with the analogous signals in the free ligand. A $^{13}$C–$^1$H heteronuclear correlation spectrum was then run to assign unambiguously the signals due to all the protonated carbons [75.1 C(3), 97.4 C(6)] in the $^{13}$C NMR spectrum. For the quaternary carbons, the peak at $\delta_C$ 232.9 was due to the three carbonyl ligands while that at 163.0 was due to the amide carbonyl carbon; four aromatic carbons [C(1), C(2), C(4) and C(5)] remained to be assigned. However, only three peaks [97.9? C(4), 108.3 C(1), 138.8 C(2)] were observed in the $^{13}$C NMR (100 MHz) (quaternary carbons only) spectrum. This could be due to the overlapping of the signal due to C(5) with that due to C(6) at 97.4. With regard to this, the literature contains a recent (Keller & Szczenski, 1988) report of the synthesis of two other tricarbonylchromium(0) complexes of aromatic tertiary amides, together with their $^{13}$C NMR data. In both there are pairs of carbons of very similar chemical shift, supporting the inference of accidental equivalence in the present case. In order to resolve this matter we have determined the crystal structure.

Diffractometer crystal 0.10 × 0.14 × 0.35 mm, lemon-coloured parallepiped, mounted on Nonius CAD-4 diffractometer; Nickel-filtered Cu $K\alpha$ radiation; unit-cell dimensions from 25 reflections $24.2 < \theta < 32.0°$; no systematic absences; space group $P\bar{1}$ by intensity statistics and satisfactory structure deter-

---

* Author to whom correspondence should be addressed.

0108-2701/92/040636-03$03.00

Table 1. *Atomic positions and thermal parameters, with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{8}{3}\pi^2(a^{*2}U_{11}^2 + b^{*2}U_{22}^2 + c^{*2}U_{33}^2 + 2a^*b^*\cos\gamma U_{12} + 2a^*c^*\cos\beta^* U_{13} + 2b^*c^*\cos\alpha U_{23}).$$

| | $x$ | $y$ | $z$ | $B_{eq}$ (Å$^2$) |
|---|---|---|---|---|
| Cr | 0.75017 (3) | 0.72436 (3) | 0.00042 (6) | 2.65 (2) |
| O(1) | 0.39960 (17) | 0.87978 (17) | −0.0796 (3) | 4.09 (10) |
| O(2) | 0.57746 (16) | 0.60720 (14) | 0.1697 (3) | 3.67 (8) |
| O(3) | 0.6609 (3) | 0.5670 (2) | −0.3081 (4) | 6.67 (17) |
| O(4) | 0.6525 (3) | 0.89903 (19) | −0.3075 (3) | 5.58 (13) |
| O(5) | 1.0101 (2) | 0.6310 (2) | −0.1288 (4) | 6.23 (14) |
| N(1) | 0.35359 (18) | 0.84568 (17) | 0.2018 (3) | 3.19 (10) |
| C(1) | 0.5856 (2) | 0.78933 (18) | 0.1714 (4) | 2.79 (10) |
| C(2) | 0.6533 (2) | 0.67190 (18) | 0.2070 (4) | 2.91 (11) |
| C(3) | 0.7920 (2) | 0.6294 (2) | 0.2723 (4) | 3.23 (11) |
| C(4) | 0.8641 (2) | 0.7022 (2) | 0.3121 (4) | 3.16 (12) |
| C(5) | 0.7970 (2) | 0.8208 (2) | 0.2867 (3) | 2.93 (10) |
| C(6) | 0.6585 (2) | 0.86121 (19) | 0.2113 (4) | 2.84 (10) |
| C(7) | 0.4376 (2) | 0.84091 (18) | 0.0874 (4) | 2.94 (10) |
| C(8) | 0.2112 (2) | 0.9043 (2) | 0.1229 (5) | 4.03 (13) |
| C(9) | 0.3927 (3) | 0.8181 (3) | 0.4118 (4) | 3.88 (13) |
| C(10) | 0.1515 (3) | 0.8324 (4) | −0.0270 (7) | 5.62 (20) |
| C(11) | 0.3390 (4) | 0.7344 (4) | 0.4602 (7) | 5.71 (19) |
| C(12) | 0.6446 (3) | 0.4860 (2) | 0.1932 (6) | 4.81 (16) |
| C(13) | 1.0132 (3) | 0.6511 (3) | 0.3864 (6) | 4.48 (17) |
| C(14) | 0.8683 (3) | 0.9032 (3) | 0.3379 (5) | 4.12 (14) |
| C(15) | 0.6950 (3) | 0.6291 (2) | −0.1892 (4) | 3.93 (12) |
| C(16) | 0.6901 (3) | 0.8327 (2) | −0.1877 (4) | 3.61 (12) |
| C(17) | 0.9090 (3) | 0.6674 (2) | −0.0794 (4) | 3.93 (13) |

Table 2. *Bond distances* (Å) *and angles* (°), *with e.s.d.'s in parentheses*

| | | | |
|---|---|---|---|
| C(1)—Cr | 2.239 (2) | C(7)—N(1) | 1.337 (3) |
| C(2)—Cr | 2.270 (2) | C(8)—N(1) | 1.470 (3) |
| C(3)—Cr | 2.226 (2) | C(9)—N(1) | 1.462 (4) |
| C(4)—Cr | 2.222 (2) | C(2)—C(1) | 1.415 (3) |
| C(5)—Cr | 2.248 (2) | C(6)—C(1) | 1.403 (3) |
| C(6)—Cr | 2.200 (2) | C(7)—C(1) | 1.519 (3) |
| C(15)—Cr | 1.827 (3) | C(3)—C(2) | 1.406 (3) |
| C(16)—Cr | 1.842 (3) | C(4)—C(3) | 1.407 (3) |
| C(17)—Cr | 1.821 (3) | C(5)—C(4) | 1.415 (3) |
| C(7)—O(1) | 1.231 (3) | C(13)—C(4) | 1.518 (3) |
| C(2)—O(2) | 1.354 (3) | C(6)—C(5) | 1.414 (3) |
| C(12)—O(2) | 1.442 (3) | C(14)—C(5) | 1.504 (3) |
| C(15)—O(3) | 1.164 (3) | C(10)—C(8) | 1.498 (5) |
| C(16)—O(4) | 1.149 (3) | C(11)—C(9) | 1.509 (4) |
| C(17)—O(5) | 1.154 (3) | | |

| | | | |
|---|---|---|---|
| C(12)—O(2)—C(2) | 117.4 (2) | C(13)—C(4)—C(5) | 121.5 (2) |
| C(8)—N(1)—C(7) | 116.9 (2) | C(6)—C(5)—C(4) | 117.9 (2) |
| C(9)—N(1)—C(7) | 124.7 (2) | C(14)—C(5)—C(4) | 122.0 (2) |
| C(9)—N(1)—C(8) | 117.2 (2) | C(14)—C(5)—C(6) | 120.0 (2) |
| C(6)—C(1)—C(2) | 118.7 (2) | C(5)—C(6)—C(1) | 122.5 (2) |
| C(7)—C(1)—C(2) | 122.9 (2) | N(1)—C(7)—O(1) | 122.6 (2) |
| C(7)—C(1)—C(6) | 118.4 (2) | C(1)—C(7)—O(1) | 119.1 (2) |
| C(1)—C(2)—O(2) | 116.1 (2) | C(1)—C(7)—N(1) | 118.2 (2) |
| C(3)—C(2)—O(2) | 124.4 (2) | C(10)—C(8)—N(1) | 113.4 (2) |
| C(3)—C(2)—C(1) | 119.5 (2) | C(11)—C(9)—N(1) | 113.7 (3) |
| C(4)—C(3)—C(2) | 121.3 (2) | O(3)—C(15)—Cr | 179.0 (3) |
| C(5)—C(4)—C(3) | 120.0 (2) | O(4)—C(16)—Cr | 178.9 (2) |
| C(13)—C(4)—C(3) | 118.5 (2) | O(5)—C(17)—Cr | 179.6 (2) |

mination and refinement; 3158 unique reflections; $\omega/2\theta$ scans, $1 \leq \theta \leq 70°$, $(\sin\theta/\lambda)_{max} = 0.6095$ Å$^{-1}$, 2738 with $I > 3.0\sigma(I)$; $-13 \leq h \leq 13$, $-15 \leq k \leq 15$, $0 \leq l \leq 8$; three intensity standards checked every 100 reflections showed no non-statistical variation during data collection; Lorentz and polarization corrections applied, absorption corrections by empirical $\psi$-scan data, maximum and minimum correction factors 0.9955 and 0.8328 respectively. The structure was solved by Patterson and difference Fourier maps. $F_{obs}$ refinement of atomic positions, non-hydrogen atoms assigned anisotropic thermal parameters, hydrogen atoms located in difference map and refined individually. Final weight $w = 1/[\sigma^2(F) + 2.04 \times 10^{-3}F^2]$, $R = 0.037$, $wR = 0.042$, $S = 1.06$; $\Delta/\sigma_{max} = 0.14$ for all positions, maximum and minimum $\Delta\rho$ excursions in final difference map 0.40 and $-0.56$ e Å$^{-3}$ respectively; atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99, 149). Calculations performed with the Enraf–Nonius (1981) *Structure Determination Package* on a PDP-11 computer for initial data reduction and with *SHELX76* (Sheldrick, 1976) on the University of Auckland IBM 4341 computer for refinement. Diagrams were produced using *ORTEP* (Johnson, 1965).

**Discussion.** Atomic coordinates for non-hydrogen atoms are listed in Table 1.* Bond distances and angles are given in Table 2. The atomic numbering and molecular geometry are shown in Fig. 1.

The complex exhibits the 'piano-stool' structure typical of ($\eta^6$-arene)tricarbonylchromium(0) compounds such as $Cr(CO)_3(\eta^6$-benzene) (Rees & Coppens, 1973) and $Cr(CO)_3(\eta^6$-toluene) (van Meurs & van Koningsveld, 1977). The $Cr(CO)_3$ tripod is eclipsed towards C(2), C(4) and C(6). This is not unexpected because the tripod then sits in such a way that it avoids unfavourable stereoelectronic interactions with the *N*,*N*-diethylcarboxamido group.

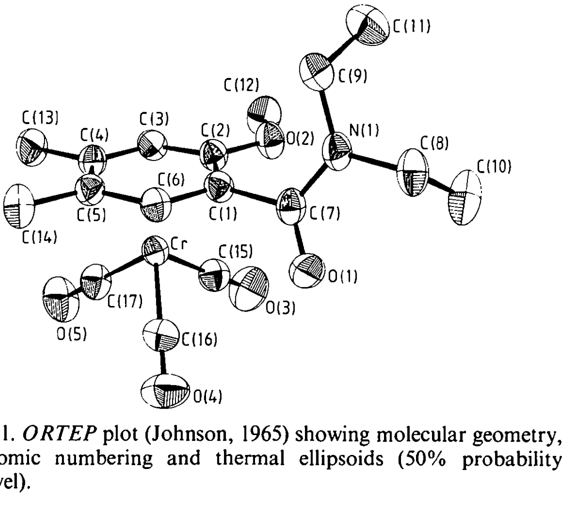


Fig. 1. *ORTEP* plot (Johnson, 1965) showing molecular geometry, atomic numbering and thermal ellipsoids (50% probability level).

---

* Lists of structure factors, thermal parameters and H-atom positions have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54596 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

[A similar conformation has been reported for the Cr(CO)$_3$ complex of 2-methoxyacetophenone (Dusausoy, Protas, Bensancon & Tirouflet, 1973).] The aromatic ring is symmetrically bonded to the chromium atom with an average Cr—C$_{\rm arene}$ bond length of 2.23 Å typical of ($\eta^6$-arene)tricarbonylchromium(0) complexes. Likewise, the average Cr—C$_{\rm co}$ bond length of 1.83 Å and the average C—O bond length of 1.15 Å are typical values. Interestingly, it is observed that the methoxy and both methyl substituents remain in the plane of the ring, whereas the C(7)—N(1) bond of the amide substituent is nearly perpendicular to the plane of the ring. Moreover, C(9) in one of the ethyl groups bonded to N(1) points back towards and above the aromatic ring while the other ethyl group faces away from the ring. These different conformations for the ethyl groups in the solid state imply different magnetic environments. Correspondingly, in the $^1$H NMR (solution phase) spectrum, the methylene protons attached to C(9) have more shielding interaction with the $\pi$-electron density of the aromatic ring, and occurred at higher field ($\delta_{\rm H}$ 3.38) than the methylene protons attached to C(8) ($\delta_{\rm H}$ 3.47). Similarly, the C(11) methyl protons resonated at higher field ($\delta_{\rm H}$ 1.13) than the C(10) methyl protons ($\delta_{\rm H}$ 1.20).

### References

CAMBIE, R. C., ERSON, A. D., GOURDIE, A. C., RUTLEDGE, P. S. & WOODGATE, P. D. (1988). *J. Organomet. Chem.* **348**, 317–331.

DUSAUSOY, Y., PROTAS, J., BENSANCON, J. & TIROUFLET, J. (1973). *Acta Cryst.* B29, 469–476.

Enraf–Nonius (1981). *Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

KELLER, A. G. & SZCZECINSKI, P. (1988). *Magn. Reson. Chem.* **26**, 990–991.

MEURS, F. VAN & VAN KONINGSVELD, H. (1977). *J. Organomet. Chem.* **131**, 423–428.

REES, B. & COPPENS, P. (1973). *Acta Cryst.* **B29**, 2516–2528.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

---

*Acta Cryst.* (1992). C**48**, 638–641

# [8,8-(PPh$_3$)$_2$-9-(OEt)-8,7-RhSB$_9$H$_9$].0.95(CH$_2$Cl$_2$)

BY MICHAEL MURPHY AND TREVOR R. SPALDING*

*Department of Chemistry, University College, Cork, Ireland*

AND GEORGE FERGUSON* AND JOHN F. GALLAGHER

*Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1*

(*Received* 10 *July* 1991; *accepted* 9 *October* 1991)

**Abstract.** 9-Ethoxy-8,8-di(triphenylphosphine)-9,10-$\mu H$-8-rhoda-7-thia-*nido*-undecaborane(10) dichloromethane solvate, C$_{38}$H$_{44}$B$_9$OP$_2$RhS.0.95(CH$_2$Cl$_2$), $M_r$ = 891.7, triclinic, $P\overline{1}$, $a$ = 10.271 (4), $b$ = 11.401 (3), $c$ = 19.426 (4) Å, $\alpha$ = 74.86 (2), $\beta$ = 88.51 (3), $\gamma$ = 83.51 (3)°, $V$ = 2182 (2) Å$^3$, $Z$ = 2, $D_x$ = 1.357 g cm$^{-3}$, graphite-monochromated Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å, $\mu$ = 6.5 cm$^{-1}$, $F$(000) = 912, $T$ = 294 K, $R$ = 0.038 for 3984 observed reflections. The title compound contains an 11-atom RhSB$_9$ *nido*-structured cage with Rh and S atoms adjacent in the open RhSB$_3$ face. An ethoxy group is bonded to the B atom adjacent to Rh in the open face with Rh—B9 2.119 (6) and B9—O 1.387 (9) Å. The phosphine ligands are bonded to the Rh atom with one Rh—P bond [2.278 (2) Å] *trans* to the S atom and the other [2.417 (1) Å] located perpendicular to the open face of the cage.

**Introduction.** We have recently described a rhodathiaborane complex which had a *nido* structure but a *closo* electron count according to Wade's rules (Ferguson, Jennings, Lough, Coughlan, Spalding, Kennedy, Fontaine & Stibr, 1990). The compound (1*a*), [8,8-(PPh$_3$)$_2$-8,7-RhSB$_9$H$_{10}$], had a gross cage geometry of a dodecahedron minus one vertex. The Rh and S atoms were adjacent and located in an open RhSB$_3$ face. One of the PPh$_3$ ligands was bonded to Rh in a position *trans* to the Rh—S vector and the other Rh—P bond was perpendicular to the open face of the cage. The P—Rh—P angle was 98.50 (2)°. We now report the structural analysis of an ethoxy derivative obtained from the reaction

---

* E-mail addresses: GF CHMFERG@VM.UOGUELPH.CA
TRS STCH8006@IRUCCVAX

0108-2701/92/040638-04$03.00