

## The Structure of Dicarbonyl[1–3a(7a)- $\eta$ -indenyl]nitrosylchromium

BY RIZ SHAKIR AND JERRY L. ATWOOD\*

Department of Chemistry, University of Alabama, University, AL 35486, USA

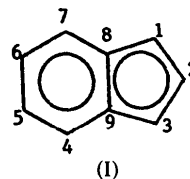
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### Abstract

( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)Cr(CO)<sub>2</sub>(NO),  $M_r = 253.2$ ,  $F(000) = 512$ , is monoclinic,  $P2_1/n$ , with  $a = 11.994(5)$ ,  $b = 7.924(4)$ ,  $c = 12.525(5)$  Å,  $\beta = 111.58(3)^\circ$ ,  $V = 1106.9$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.52$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å. The crystal structure has been refined by full-matrix least-squares techniques to an  $R$  index of 0.046 based on 1469 independent reflections measured on a diffractometer. The indenyl ligand is tilted such that the Cr–C( $\pi$ ) bond distances range from 2.177 (6) to 2.301 (9) Å. The nitrosyl and carbonyl ligands are clearly resolved in contrast to the disorder found with ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Cr(CO)<sub>2</sub>(NO).

### Introduction

Although the structure of the first transition-metal/indenyl complex, namely ( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)<sub>2</sub>Fe (Trotter, 1958), was carried out shortly after that of ferrocene itself (Dunitz, Orgel & Rich, 1956), relatively few studies on the  $\eta^5$ -coordination mode of the indenyl ligand have surfaced. This is surprising in view of the significant differences in electronic and steric effects between the indenyl and cyclopentadienyl ligands. Coordination of the C(8) and C(9) carbon atoms (I) is often impeded by the presence of the fused six-membered ring. Typically this results in a lengthening of the C(8) and C(9) carbon–metal bonds relative to those of C(1), C(2), and C(3): in ( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)<sub>3</sub>UCl (Burns & Laubereau, 1971) the averages are 2.86 vs 2.72 Å, respectively, and in ( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)<sub>2</sub>Zr(CH<sub>3</sub>)<sub>2</sub> (Atwood, Hunter, Hrcir, Samuel, Alt & Rausch, 1975), 2.61 vs 2.51 Å. The C(1) position is electron rich and this produces a tendency for stabilization of the  $\eta^1$ -coordination mode. Verification of this bonding pattern has been found in solution (Tsutsui & Gysling, 1969), and, less commonly, in the solid state (Cotton, Musco & Yagupsky, 1967). ( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)Cr(CO)<sub>2</sub>(NO) presents an excellent opportunity to study the interplay of these effects.



A second interest in the title compound concerns the dicarbonylnitrosyl tripod. Information about the  $\pi$ -bonded ligand can be obtained from an analysis of the Cr–C, Cr–N, C $\equiv$ O, and N $\equiv$ O bond lengths. Unfortunately, the CO and NO ligands are often disordered. Since this problem was not encountered with ( $\eta^5$ -C<sub>13</sub>H<sub>9</sub>)Cr(CO)<sub>2</sub>(NO) (Atwood, Shakir, Malito, Herberhold, Kremnitz, Bernhagen & Alt, 1979), it seemed worth while to investigate the indenyl analogue.

Deep-red crystals of the title complex were obtained by slow sublimation at moderate temperature, since decomposition results at higher temperatures. Single crystals were mounted in thin-walled glass capillaries. Crystallographic parameters were determined from preliminary data collected on an Enraf–Nonius CAD-4 diffractometer with graphite-crystal-monochromated Mo radiation. Lattice parameters were determined from least-squares refinement of the angular settings of 15 reflections ( $\theta > 20^\circ$ ), accurately centred on the diffractometer.

Intensity data for the  $hkl-h\bar{k}l$  quadrant were collected out to  $2\theta = 50^\circ$  by the  $\theta-2\theta$  scan technique in the previously described manner (Holton, Lappert, Ballard, Pearce, Atwood & Hunter, 1979). A total of 1474 unique observed reflections were obtained. The intensities were corrected for Lorentz and polarization effects but not for absorption.

Full-matrix, least-squares refinement was carried out using the Busing, Martin & Levy (1962) program ORFLS. The function  $\sum [w(|F_o| - |F_c|)^2]$  with a weighting scheme based on essentially unit weights was minimized. Neutral-atom scattering factors for Cr, C, O, and N were taken from the compilation of Cromer & Waber (1965); those for H were from Stewart, Davidson & Simpson (1965). The scattering for Cr was corrected for anomalous dispersion using Cromer & Liberman's (1970) table.

\* To whom correspondence should be addressed.

The position of the Cr atom was located by the inspection of a Patterson map. A difference Fourier map based on the metal atom readily revealed the positions of the remaining non-hydrogen atoms.

Four cycles of refinement with isotropic temperature factors led to an  $R$  value of 0.153. At this point, the reflections 002,  $10\bar{1}$ ,  $11\bar{1}$ ,  $20\bar{2}$ , and  $30\bar{1}$  were removed because they apparently suffered from secondary extinction. The conversion of all non-hydrogen atoms to anisotropic thermal parameters and further refinement yielded  $R_1 = \sum (|F_o| - |F_c|) / \sum |F_o| = 0.060$ ; a difference Fourier map gave good indications of the positions of the seven H atoms. Several cycles of refinement of the non-hydrogen atoms (parameters of the H atoms were not refined) gave the final agreement values of  $R_1 = 0.046$  and  $R_2 = [\sum (|F_o| - |F_c|)^2 / \sum (F_o)^2]^{1/2} = 0.051$ . The largest parameter shifts in the last cycle of refinement were less than 0.01 of their estimated standard deviations. The estimated standard deviation of an observation of unit weight is 1.10. A final difference Fourier map indicated no unaccounted electron density. No systematic variation of  $w(|F_o| - |F_c|)$  vs  $|F_o|$  or  $(\sin \theta) / \lambda$  was observed. The final atomic parameters are listed in Table 1 and bond lengths and angles in Figs. 1 and 2.\*

\* Lists of structure factors, anisotropic temperature factors, and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36031 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final fractional coordinates and thermal parameters for  $(\eta^5\text{-C}_9\text{H}_7)\text{Cr}(\text{CO})_2(\text{NO})$

Standard deviations in parentheses refer to last digit quoted.

	x	y	z	$B_{\text{eq}}$ ( $\text{\AA}^2$ )
Cr	-0.04344 (7)	0.18863 (10)	0.24784 (7)	4.01 (3)
O(1)	0.0008 (4)	-0.1246 (5)	0.3754 (3)	6.0 (2)
O(2)	0.2009 (4)	0.2012 (8)	0.2356 (5)	9.5 (3)
O(3)	-0.1699 (6)	0.0258 (6)	0.0178 (4)	10.1 (3)
N	-0.0173 (4)	0.0002 (6)	0.3224 (4)	5.0 (2)
C(1)	-0.2037 (4)	0.3063 (7)	0.2584 (5)	4.9 (2)
C(2)	-0.1103 (6)	0.3132 (9)	0.3672 (5)	5.6 (2)
C(3)	-0.0167 (5)	0.4116 (8)	0.3587 (5)	5.6 (3)
C(4)	-0.0001 (6)	0.5855 (7)	0.1846 (7)	6.1 (3)
C(5)	-0.0657 (8)	0.6255 (8)	0.0718 (8)	7.0 (3)
C(6)	-0.1812 (7)	0.5566 (9)	0.0133 (6)	6.6 (3)
C(7)	-0.2317 (5)	0.4542 (7)	0.0649 (5)	5.2 (2)
C(8)	-0.1709 (4)	0.4122 (6)	0.1810 (4)	3.8 (2)
C(9)	-0.0539 (5)	0.4786 (6)	0.2423 (5)	4.4 (2)
C(10)	0.1055 (5)	0.1944 (7)	0.2381 (5)	5.3 (2)
C(11)	-0.1201 (6)	0.0865 (7)	0.1046 (5)	6.3 (3)
H(1) C(1)	-0.2787	0.2350	0.2369	
H(2) C(2)	-0.1110	0.2572	0.4385	
H(3) C(3)	0.0624	0.4332	0.4218	
H(4) C(4)	0.0828	0.6316	0.2246	
H(5) C(5)	-0.0323	0.7037	0.0289	
H(6) C(6)	-0.2262	0.5846	-0.0706	
H(7) C(7)	-0.3131	0.4062	0.0226	

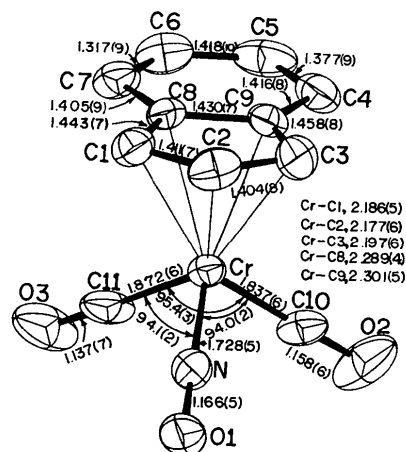


Fig. 1. Molecular structure and atom-numbering scheme for  $(\eta^5\text{-C}_9\text{H}_7)\text{Cr}(\text{CO})_2(\text{NO})$  with the atoms represented by their 50% probability ellipsoids for thermal motion.

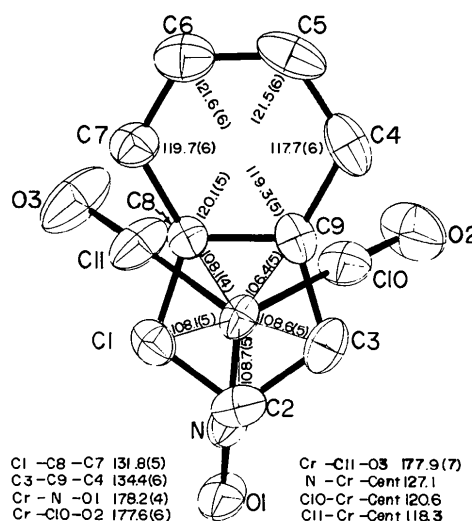


Fig. 2. Orientation of the  $(\text{CO})_2(\text{NO})$  tripod with respect to the indenyl ring.

## Discussion

A diagram of the molecular structure and atom-numbering scheme is shown in Fig. 1. Important structural parameters of the title compound are compared with those of related substances in Table 2.  $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2(\text{NO})$  (Atwood *et al.*, 1979) and  $[\eta^5\text{-C}_5(\text{CH}_3)_3]\text{Cr}(\text{CO})_2(\text{NO})$  (Malito, Shakir & Atwood, 1980) show disorder of the carbonyl and nitrosyl groups, but  $(\eta^5\text{-C}_9\text{H}_7)\text{Cr}(\text{CO})_2(\text{NO})$  and  $(\eta^5\text{-C}_{13}\text{H}_9)\text{Cr}(\text{CO})_2(\text{NO})$  (Atwood *et al.*, 1979) are crystallographically ordered. For the latter the nitrosyl group was *trans* to the electron-rich C(1) of the fluorenyl ligand (II). Thus the order could have arisen as the result of an electronic effect. In the present situation the nitrosyl is *not trans* to the C(1) position of

Table 2. Comparison of bond distances (Å) and bond angles ( $^{\circ}$ ) in selected nitrosyl complexes

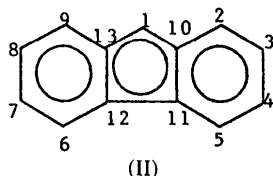
	( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )- Cr(CO) <sub>2</sub> (NO) <sup>a*</sup>	( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )- Cr(CO) <sub>2</sub> (NO) <sup>b*</sup>	( $\eta^5$ -C <sub>13</sub> H <sub>9</sub> )- Cr(CO) <sub>2</sub> (NO) <sup>a</sup>	( $\eta^5$ -C <sub>9</sub> H <sub>7</sub> )- Cr(CO) <sub>2</sub> (NO) <sup>c</sup>
Cr-N	} 1.801	} 1.805	1.687 (7)	1.728 (5)
Cr-C			1.864 (6)	1.855 (19)
Cr-Cent†	1.844	1.846	1.884	1.866
C(carbonyl)-Cr-N	} 93.3	} 94.9	95.3 (3)	94.0 (2)
C(carbonyl)-Cr-C(carbonyl)			88.4 (3)	95.4 (3)
Cent-Cr-N	} 122.9	} 121.7	128.5	127.1
Cent-Cr-C(carbonyl)			119.1	119.5

References: (a) Atwood *et al.* (1979); (b) Malito, Shakir & Atwood (1980); (c) this study.

\* The structure contains a disordered -Cr(CO)<sub>2</sub>(NO) moiety.

† Cent refers to the centroid of the five-membered ring.

the indenyl (I), and steric effects must be considered in detail.



Evidence for a significant degree of crowding in ( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)Cr(CO)<sub>2</sub>(NO) can be found from observation of several of the molecular parameters. Firstly, the Cr-C( $\eta^5$ ) bond lengths show the familiar pattern: there are three normal ones, 2.177 (6), 2.186 (5), and 2.197 (6) Å, and two longer ones, 2.289 (4) and 2.301 (5) Å. This is the situation shown in ( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)<sub>3</sub>UCl (Burns & Laubereau, 1971) and ( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)<sub>2</sub>Zr(CH<sub>3</sub>)<sub>2</sub> (Atwood *et al.*, 1975), and is in agreement with that found in the closely related ( $\eta^5$ -C<sub>9</sub>H<sub>6</sub>Br)Mn(CO)<sub>3</sub> (Honan, Atwood, Bernal & Herrmann, 1979). In the latter the values are 2.125 (5), 2.128 (9), 2.130 (10), 2.205 (9), and 2.222 (9) Å. Secondly, the Cr-centroid distance is 1.866 Å in the indenyl complex, while it is 1.844 and 1.846 Å in the cyclopentadienyl and pentamethylcyclopentadienyl compounds, respectively. Thirdly, the nitrosyl ligand is positioned essentially *trans* to the six-membered ring (Fig. 2). Since the Cr-N bond length, 1.728 (5) Å, is shorter than the average Cr-C(carbonyl) distance, 1.855 (19) Å, it would be expected to reside farthest from the source of the nonbonded repulsion.

Although the indenyl ring system does present a considerable steric problem, there are several more subtle electronic effects evident in the dicarbonyl-nitrosyl tripod. The C-Cr-C and C-Cr-N bond angles are on the average (94.9 $^{\circ}$ ) larger than those found in ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Cr(CO)<sub>2</sub>(NO) (Atwood *et al.*, 1979), 93.3 $^{\circ}$ . Since the expansion of these angles is in opposition to the decrease demanded by steric considerations, the change of 1.6 $^{\circ}$  per angle must be quite significant. An average of 94.9 $^{\circ}$  was also found

with the [ $\eta^5$ -C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>]Cr(CO)<sub>2</sub>(NO) structure and was attributed indirectly to the added electron density on the cyclopentadienyl ring due to the presence of the electron-releasing methyl groups.

Careful scrutiny of Figs. 1 and 2 shows that C(10) is almost exactly *trans* to the C(1) position on the indenyl ring. This leads to a strengthening of the Cr-C(10) bond, 1.837 (6) Å, compared to Cr-C(11), 1.872 (6) Å. The effect is also reflected in the longer C(10)-O(2) length, 1.158 (6) Å, and shorter C(11)-O(3) distance, 1.137 (7) Å. The Cr-C-O angle of 177.8 (9) $^{\circ}$  indicates the usual mode of bonding for a terminal carbonyl in a metal complex.

The average of the three shortest Cr-C( $\eta^5$ ) bond lengths, 2.187 (9) Å, agrees well with the related values of 2.188 (5) Å in ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Cr(CO)<sub>2</sub>(NO) and 2.20 (1) Å in [( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Cr(CO)<sub>3</sub>]<sub>2</sub> (Adams, Collins & Cotton, 1974).

The Cr-N length, 1.728 (5) Å, is significantly larger than that found for ( $\eta^5$ -C<sub>13</sub>H<sub>9</sub>)Cr(CO)<sub>2</sub>(NO), 1.687 (7) Å. However, in the latter, the nitrosyl ligand was *trans* to the C(1) position of the fluorenyl group. The value observed for the title compound agrees well with the 1.72 (1) Å length found in ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Cr(NO)<sub>2</sub>(NCO) (Bush & Sim, 1970). The N≡O length is 1.166 (5) Å in the indenyl complex and 1.169 (9) Å in the fluorenyl derivative. The Cr-N-O angle of 178.2 (4) $^{\circ}$  conforms with the NO<sup>+</sup> formulation for M-N-O linkages.

An interesting difference between the title compound and its fluorenyl analogue involves the least-squares planes of the  $\pi$ -bonded ligands. For the former there is a readily accessible mode of relief of the nonbonded intramolecular repulsion: a tilt of the entire indenyl group. Thus, the cyclopentadienyl fragment is planar to within 0.021 Å, while the maximum deviation for the ligand itself is only 0.035 Å. The Cr...cyclopentadienyl-plane distance is 1.866 Å, and the Cr...ligand-plane separation is 1.865 Å. Such is not the case for the fluorenyl ligand. Here the cyclopentadienyl moiety is planar to within 0.032 Å and the ligand itself, 0.072 Å. The Cr atom is 0.045 Å closer to the plane of the

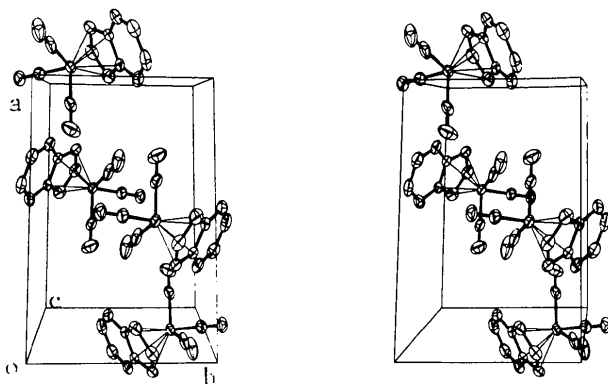


Fig. 3. Stereoscopic view of the unit-cell packing in  $(\eta^5\text{-C}_9\text{H}_7)\text{Cr}(\text{CO})_2(\text{NO})$ .

five-membered ring than to the plane of the entire ligand.

A stereoscopic view of the unit-cell contents is shown in Fig. 3. No unusually close intermolecular contacts are observed, but it is interesting to note that the indenyl ligands on adjacent molecules are neighbors, while the  $(\text{XO})_3$  (where  $\text{X} = \text{N}$  or  $\text{C}$ ) tripods are stacked in an interlocking fashion. This same packing mode was observed for  $(\eta^5\text{-C}_{13}\text{H}_9)\text{Cr}(\text{CO})_2(\text{NO})$  (Atwood *et al.*, 1979).

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## Structures of the Sodium-*p*-Terphenyl Ion Pairs: Disodium Terphenylide-Tetrahydrofuran (1/6) and Disodium Diterphenylide Terphenyl-1,2-Dimethoxyethane (1/6)

BY J. H. NOORDIK, H. M. DOESBURG AND P. A. J. PRICK

*Crystallography Laboratory, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands*

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### Abstract

The crystal structures of  $2\text{Na}^+\cdot\text{C}_{18}\text{H}_{14}^{\ominus}\cdot 6\text{C}_4\text{H}_8\text{O}$  [ $\text{Na}_2\text{tp}(\text{H}_4\text{furan})_6$ ] and  $2\text{Na}^+\cdot 2\text{C}_{18}\text{H}_{14}^{\ominus}\cdot\text{C}_{18}\text{H}_{14}\cdot 6\text{C}_4\text{H}_8\text{O}_2$  ( $\text{Na}_2\text{tp}_3\cdot\text{dme}_6$ ) have been determined by X-ray diffraction at room temperature and 130 K respectively.  $\text{Na}_2\text{tp}(\text{H}_4\text{furan})_6$ :  $M_r = 708.6$ , mono-

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