

## THE PREPARATION AND CRYSTAL STRUCTURES OF DICARBONYLCYCLOPENTADIENYLNITROSYLCHROMIUM AND DICARBONYLFLUORENYLNITROSYLCHROMIUM

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### Summary

The X-ray-crystal structures of both  $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2(\text{NO})$  (I) and  $(\eta^5\text{-C}_{13}\text{H}_9)\text{-Cr}(\text{CO})_2(\text{NO})$  (II,  $\eta^5\text{-C}_{13}\text{H}_9 = \eta^5\text{-9H-fluorenyl}$ ) are described. I crystallizes in the monoclinic space group  $P2_1/n$  with lattice constants  $a$  10.998(4),  $b$  7.066(3),  $c$  11.940(4) Å,  $\beta$  116.37(4)°, and  $\rho_{\text{calc}}$  1.63 g cm<sup>-3</sup> for  $Z = 4$ . II belongs to the orthorhombic space group  $Pnma$  with  $a$  6.463(4),  $b$  15.512(6),  $c$  12.916(6) Å, and  $\rho_{\text{calc}}$  1.55 g cm<sup>-3</sup> for  $Z = 4$ . Least-squares refinement gave final conventional  $R$  values of 0.037 based on 1081 independent observed reflections for I, and 0.042 with 630 reflections for II. The carbonyl and nitrosyl groups are disordered in I, but the nitrosyl ligand in II occupies a position "trans" to the electron-rich C(9) of the fluorenyl system. Photolysis of II in liquid olefins (L) or acetylenes leads to substituted derivatives of the type  $(\eta^5\text{-C}_{13}\text{H}_9)\text{Cr}(\text{CO})\text{-}(\text{NO})\text{L}$  (L = cyclooctene, cycloocta-1,5-diene, norbornene, norbornadiene, phenylacetylene).

### Introduction

While the chemistry of the well-known dicarbonylcyclopentadienylnitrosyl complexes of chromium, molybdenum and tungsten has recently become the subject of considerable study [1], the solid state structures of these complexes have been completely ignored. To date, the only structurally characterized cyclopentadienylnitrosyl-containing complexes of chromium are  $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2\text{X}$  (X = Cl [2] or NCO [3]),  $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})\text{X}]_2$  (X = SPh [4] or NMe<sub>2</sub> [5]),  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{NO})_3(\text{NH})_2$  [6] and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2]_2$  [7]. Furthermore,

the use of cyclopentadienyl congeners in the above dicarbonylnitrosyl compounds has not been previously considered. Herein, we report the X-ray crystal structures of both  $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2(\text{NO})$  (I) and the novel  $(\eta^5\text{-C}_{13}\text{H}_9)\text{Cr}(\text{CO})_2(\text{NO})$  (II,  $\eta^5\text{-C}_{13}\text{H}_9 = \eta^5\text{-9H-fluorenyl}$ ). The synthesis of the fluorenyl complex II and of some derivatives is also described.

## Experimental

### A. Synthetic studies

All reactions were carried out under an atmosphere of dry nitrogen. The solvents were dried (THF and n-pentane over sodium wire,  $\text{CH}_2\text{Cl}_2$  over  $\text{P}_4\text{O}_{10}$ ) and redistilled before use in a stream of nitrogen.

*Preparation of dicarbonyl( $\eta^5$ -fluorenyl)nitrosylchromium,  $(\eta^5\text{-C}_{13}\text{H}_9)\text{Cr}(\text{CO})_2(\text{NO})$  (II).* A THF solution (ca. 5 ml) of 1.9 mmol nitrosyl chloride,  $\text{ClNO}$ , was added dropwise to a solution of 512 mg (2 mmol) tricarbonyl(mesitylene)chromium,  $(\text{C}_6\text{H}_3\text{Me}_3)\text{Cr}(\text{CO})_3$ , in 50 ml THF at  $-78^\circ\text{C}$ . Evolution of CO took place and the solution assumed the red colour of the intermediate  $[\text{CrCl}(\text{CO})_2(\text{NO})] \cdot x \text{ THF}$  [8]. A THF solution (20 ml) of excess fluorenyllithium (3 mmol, prepared from fluorene and  $\text{CH}_3\text{Li}/(\text{C}_2\text{H}_5)_2\text{O}$ ) was then added at  $-78^\circ\text{C}$ , and the reaction mixture was stirred for 2 h at  $-78^\circ\text{C}$ . After thawing and filtration, the red-brown filtrate was evaporated to dryness and the residue extracted several times with n-pentane until the solution remained colorless. The combined pentane extracts were concentrated and chromatographed on alumina with  $\text{CH}_2\text{Cl}_2$  for elution. The red eluate was concentrated, diluted with n-pentane and cooled to  $-30^\circ\text{C}$ . Recrystallization of the red product from n-pentane gave dark-red needles of  $(\eta^5\text{-C}_{13}\text{H}_9)\text{Cr}(\text{CO})_2(\text{NO})$  (II), m.p.  $115^\circ\text{C}$  (under  $\text{N}_2$ ). Yield 150–200 mg (25–33%). Mol. weight 303, by mass spectroscopy (calcd. 303.24).

Preparation of  $(\eta^5\text{-C}_{13}\text{H}_9)\text{Cr}(\text{CO})(\text{NO})\text{L}$  complexes (Table 1), (L = cyclooctene,

TABLE I  
FLUORENYL COMPLEXES OF THE TYPE  $(\eta^5\text{-C}_{13}\text{H}_9)\text{Cr}(\text{CO})(\text{NO})\text{L}$

Ligand L	M.p. ( $^\circ\text{C}$ ) (under $\text{N}_2$ )	Infrared <sup>a</sup>		Elemental analysis (Found (calcd.) (%))			
		$\nu(\text{CO})$ ( $\text{cm}^{-1}$ )	$\nu(\text{NO})$ ( $\text{cm}^{-1}$ )	C	H	N	Cr
Carbon monoxide (II)	115	2022, 1955	1713	59.05 (59.41)	3.11 (2.99)	4.42 (4.62)	16.97 (17.15)
Cyclooctene	103	1967	1680	68.62 (68.56)	5.98 (6.02)	3.79 (3.63)	13.53 (13.49)
Cycloocta-1,5-diene		1970	1681	68.55 (68.92)	5.70 (5.52)	3.88 (3.52)	13.63 (13.56)
Norbornene	93 (dec.)	1969	1687	68.15 (68.28)	5.31 (5.18)	3.92 (3.79)	14.39 (14.08)
Norbornadiene	76 (dec.)	1970	1688	68.40 (68.66)	4.80 (4.66)	3.73 (3.81)	14.10 (14.15)
Phenylacetylene	85 (dec.)	2001	1687	69.75 (70.02)	4.22 (4.01)	3.50 (3.71)	13.87 (13.78)

<sup>a</sup> n-Pentane solution.

cycloocta-1,5-diene, norbornene, norbornadiene, phenylacetylene): 303 mg (1 mmol)  $(\eta^5\text{-C}_{13}\text{H}_9)\text{Cr}(\text{CO})_2(\text{NO})$  (II) were dissolved in ca. 10 ml of the unsaturated hydrocarbon, L, and the solution was irradiated by a mercury lamp (Hanovia S-200W) until the  $\nu(\text{CO})$  absorptions of II had completely disappeared in the IR solution spectrum (ca. 1–4 h). (In the case of norbornene, the olefin was diluted with 5 ml benzene). The reaction mixture was then brought to dryness at 0.1 Torr, the residue recrystallized from n-pentane and the red complex eventually dried in a high vacuum at room temperature. The yields varied in the range of 30–60%.

### B. Crystal structure analyses

Preparation of crystals for the X ray studies: Good crystals of both  $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2(\text{NO})$  (I) and  $(\eta^5\text{-C}_{13}\text{H}_9)\text{Cr}(\text{CO})_2(\text{NO})$  (II) were obtained by slow crystallization from n-pentane.

1. *Dicarbonylcyclopentadienylnitrosylchromium (I)*. Single crystals of the compound were sealed in thin-walled glass capillaries. Final parameters as determined from a least-squares refinement of the angular settings of 15 reflections ( $2\theta > 20^\circ$ ) accurately on an Enraf-Nonius CAD-4 diffractometer are given in Table 2. The space group was determined to be  $P2_1/n$  from systematic absences:  $h0l, h + l = 2n + 1; 0k0, k = 2n + 1$ .

Data were collected on the diffractometer with graphite crystal monochromated  $\text{Mo-K}_\alpha$  radiation. The diffracted intensities were collected by the  $\omega - 2\theta$  scan technique with a takeoff angle of  $3.5^\circ$ . The scan rate was variable and was determined by a fast  $20^\circ \text{ min}^{-1}$  prescan. Calculated speeds for the slow scan (based on the net intensity gathered in the prescan) ranged from 20 to  $0.3^\circ \text{ min}^{-1}$ . Other diffractometer parameters and the method of estimation of standard deviations have been previously described [9]. As a check on the stability of the instrument and crystal, the (004) and (040) reflections were measured after every 50 reflections; no significant variation was noted.

One independent quadrant of data was measured out to  $2\theta 50^\circ$ ; a slow scan

(continued on p. 70)

TABLE 2  
CRYSTAL DATA<sup>a</sup>

	$(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2(\text{NO})$ (I)	$(\eta^5\text{-C}_{13}\text{H}_9)\text{Cr}(\text{CO})_2(\text{NO})$ (II)
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	$Pnma$
Mol. wt.	203.1	303.2
<i>a</i>	10.998(4) Å	6.463(4) Å
<i>b</i>	7.066(3) Å	15.512(6) Å
<i>c</i>	11.940(4) Å	12.916(6) Å
$\beta$	116.37(4) <sup>o</sup>	—
Cell volume	831.3 Å <sup>3</sup>	1294.9 Å <sup>3</sup>
Molecules/unit cell	4	4
Calc. density	1.63	1.55
Linear abs. coeff., $\mu$	14.0 cm <sup>-1</sup>	9.27 cm <sup>-1</sup>
Max. crystal dim.	0.30 × 0.65 × 0.65 mm	0.25 × 0.40 × 0.70 mm

<sup>a</sup>  $\text{Mo-K}_\alpha$  radiation,  $\lambda 0.71069$  Å. Ambient temperature of  $23 \pm 1^\circ\text{C}$ .

TABLE 3  
FINAL FRACTIONAL COORDINATES AND ANISOTROPIC THERMAL PARAMETERS<sup>a</sup> FOR  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}(\text{CO})_2(\text{NO})$  (I)

Atom	x/a	y/b	z/c	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Cr	0.47657(7)	0.01863(10)	0.71408(7)	0.00967(7)	0.0186(2)	0.01150(8)	-0.0013(1)	0.00497(6)	0.0003(1)
O(1)	0.3940(5)	0.3113(6)	0.5148(4)	0.0280(8)	0.028(1)	0.0141(5)	-0.0022(7)	0.0077(5)	0.0043(6)
O(2)	0.5612(4)	0.3012(6)	0.3132(3)	0.0181(5)	0.041(1)	0.0135(4)	-0.0035(7)	0.0068(4)	-0.0084(6)
O(3)	0.7539(4)	-0.0289(6)	0.7335(4)	0.0121(4)	0.043(1)	0.0299(7)	-0.0050(6)	0.0128(5)	-0.0115(8)
X(1)	0.4273(5)	0.1958(7)	0.6919(4)	0.0155(6)	0.023(1)	0.0116(5)	-0.0034(7)	0.0058(5)	-0.0013(6)
X(2)	0.5287(4)	0.1896(6)	0.8337(4)	0.0104(5)	0.026(1)	0.0094(4)	-0.0013(6)	0.0044(4)	-0.0020(6)
X(3)	0.6472(4)	-0.0090(7)	0.7252(4)	0.0131(5)	0.024(1)	0.0169(6)	-0.0035(7)	0.0081(5)	-0.0049(7)
C(1)	0.4468(5)	-0.2880(7)	0.6952(7)	0.0139(7)	0.017(1)	0.028(1)	-0.0007(7)	0.0132(8)	-0.0007(9)
C(2)	0.4452(6)	-0.2312(8)	0.8062(6)	0.0146(7)	0.028(1)	0.0162(7)	-0.0012(8)	0.0047(6)	0.0089(8)
C(3)	0.3337(6)	-0.1131(8)	0.7729(6)	0.0161(7)	0.026(1)	0.0182(6)	-0.0025(8)	0.0114(7)	0.0017(9)
C(4)	0.2713(5)	-0.0959(7)	0.6456(6)	0.0087(5)	0.022(1)	0.0211(9)	-0.0016(6)	0.0042(6)	0.0045(8)
C(5)	0.3417(6)	-0.2032(8)	0.6952(5)	0.0175(8)	0.028(1)	0.0150(7)	-0.0102(9)	0.0075(7)	-0.0048(8)
H(1)[C(1)]	0.5072	-0.3625	0.8889	5.0000					
H(2)[C(2)]	0.5043	-0.2617	0.8894	5.0000					
H(3)[C(3)]	0.3105	-0.0578	0.8370	5.0000					
H(4)[C(4)]	0.1937	-0.0237	0.5935	5.0000					
H(5)[C(5)]	0.3196	-0.2097	0.5041	5.0000					

<sup>a</sup> Anisotropic thermal parameters defined by  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ .

TABLE 4

FINAL FRACTIONAL COORDINATES AND THERMAL PARAMETERS<sup>a</sup> FOR ( $\eta^5$ -C<sub>13</sub>H<sub>9</sub>)Cr(CO)<sub>2</sub>(NO) (II)

Atom	x/a	y/b	z/c	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Cr	0.19307(21)	0.25000	0.04550(9)	0.02198(33)	0.00321(5)	0.00312(6)	0.000000	0.00019(17)	0.0000
O(1)	-0.2141(11)	0.2500	0.1314(5)	0.0213(20)	0.0145(6)	0.0070(5)	0.0000	0.0005(9)	0.0000
O(2)	0.3660(7)	0.3855(2)	0.1880(3)	0.0469(19)	0.0046(2)	0.0068(3)	-0.0031(5)	-0.0021(6)	-0.0020(2)
N	-0.0467(12)	0.2500	0.0971(5)	0.0219(23)	0.0072(5)	0.0051(5)	0.0000	0.0016(9)	0.0000
C(1)	0.4494(12)	0.2500	-0.0645(6)	0.0234(24)	0.0039(4)	0.0038(5)	0.0000	0.0000(9)	0.0000
C(2)	0.3265(10)	0.1760(3)	-0.0884(4)	0.0232(18)	0.0035(2)	0.0032(3)	0.0014(6)	0.0010(6)	-0.0003(2)
C(3)	0.1232(8)	0.2035(3)	-0.1174(4)	0.0238(18)	0.0031(2)	0.0033(3)	-0.0003(5)	-0.0002(6)	-0.0002(2)
C(4)	0.3732(10)	0.0853(4)	-0.0856(4)	0.0346(23)	0.0038(3)	0.0047(4)	0.0031(7)	0.0000(7)	-0.0004(3)
C(5)	0.2200(14)	0.0292(4)	-0.1123(4)	0.0516(30)	0.0033(3)	0.0055(4)	0.0017(8)	0.0004(10)	-0.0010(3)
C(6)	0.0201(12)	0.0562(4)	-0.1420(5)	0.0454(28)	0.0042(3)	0.0054(5)	-0.0026(8)	-0.0003(9)	-0.0012(3)
C(7)	-0.0313(10)	0.1423(4)	-0.1447(4)	0.0264(20)	0.0048(3)	0.0043(4)	-0.0015(6)	-0.0012(7)	-0.0006(3)
C(8)	0.2987(10)	0.3338(3)	0.1344(4)	0.0281(17)	0.0035(2)	0.0039(3)	0.0011(7)	-0.0006(8)	0.0006(2)
H1(C1)	0.595	0.250	-0.034 <sup>b</sup>						
H2(C4)	0.515	0.063	-0.063						
H3(C5)	0.252	-0.035	-0.111						
H4(C6)	-0.086	0.010	-0.160						
H5(C7)	-0.178	0.162	-0.165						

<sup>a</sup> Anisotropic temperature factors of the form  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ . <sup>b</sup> Hydrogen atoms were placed in calculated positions with B 5.0 Å<sup>2</sup>.

was performed on a total of 1081 unique reflections. Since these data were scanned at a speed which yielded a net count of 3000, the calculated standard deviations were all very nearly equal. No reflection was subjected to a slow scan unless a net count of 35 or more was obtained in the prescan. Based on these considerations, the data set of 1081 reflections (used in the subsequent structure determination and refinement) was considered observed, and consisted in the main of those for which  $I > 3\sigma(I)$ . The intensities were corrected for Lorentz and polarization effects, but not for absorption, since the value of  $\mu$  is  $14.0 \text{ cm}^{-1}$ .

The function  $w(|F_0| - |F_c|)^2$  was minimized [10]. No corrections were made for extinction. Neutral atom scattering factors were taken from the compilations of Cromer and Waber [11] for Cr, O, N and C; those for H were from International Tables for X-ray Crystallography [12].

The existence of four molecules per unit cell in the space group  $P2_1/n$  meant that the molecule possesses no crystallographically imposed symmetry. Interpretation of the Patterson map gave the position of the chromium atom, and a subsequent difference Fourier afforded the coordinates of the remaining non-hydrogen atoms. The carbon and nitrogen atoms of the X=O ligands were initially treated as carbon atoms. Least-squares refinement with isotropic temperature factors yielded  $R_1 = \Sigma(|F_0| - |F_c|)/\Sigma|F_0| = 0.095$ . At this point it was clear from the examination of the thermal parameters and the bond lengths within the  $\text{Cr}(\text{CO})_2(\text{NO})$  unit, that the carbonyl and nitrosyl ligands were disordered in such a way as to occupy each of the three equivalent positions one third of the time. A weighted scattering factor ( $\frac{2}{3}f_C + \frac{1}{3}f_N$ ) was adopted for the disordered atoms. Conversion to anisotropic thermal parameters and further refinement gave  $R_1 = 0.048$ . The five hydrogens on the cyclopentadienyl ring were placed at calculated positions and more cycles of least-squares refinement gave  $R_1 = 0.038$  and  $R_2 = [\Sigma w(|F_0| - |F_c|)^2/\Sigma|F_0|^2]^{1/2} = 0.038$ . The weighting scheme was based on unit weights, and unobserved reflections were not included. The largest parameter shifts in the final cycle of refinement were less than 0.05 of their estimated standard deviations. The estimated standard deviation of an observation of unit weight was 1.28. A final difference Fourier map showed no unaccounted electron density. The final values of the positional and thermal parameters are given in Table 3.

2. *Dicarbonylfluorenylnitrosylchromium (II)*. The final lattice parameters determined as above are given in Table 2. The space group was found to be  $Pnma$  or  $Pn2_1a$  from systematic absences:  $0kl, k + l = 2n + 1; hk0, h = 2n + 1$ .

The data collection procedure was as given above except that the calculated speed of the slow scans varied from 20 to  $0.5^\circ \text{ min}^{-1}$ ; the data were scanned at a speed which yielded a net count of 4000, and a slow scan was only performed if a net count of 20 or more was gathered in the prescan. From similar considerations to those in I a total of 630 reflections were observed and were used in the structure solution and refinement. The intensities were corrected for Lorentz and polarization effects but not for absorption ( $\mu 9.27 \text{ cm}^{-1}$ ).

A value for  $Z$  of four in the space group  $Pn2_1a$  demanded no crystallographic symmetry, while  $Pnma$  required the molecule to reside on either a mirror plane or a center of inversion. Subsequent structure solution and refinement showed that the correct choice is  $Pnma$ . Interpretation of a Patterson map gave the

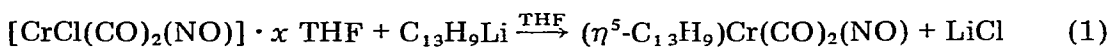
position of the chromium atom, and the resulting difference Fourier afforded the coordinates of the remaining nonhydrogen atoms. No indication of disorder was observed in this case. Least-squares refinement with isotropic temperature factors yielded  $R_1 = 0.074$ . Conversion to anisotropic thermal parameters and further refinement gave  $R_1 = 0.042$ . The placement of the five symmetry independent hydrogen atoms in calculated positions and additional least-squares refinement led to final values of  $R_1 = 0.038$  and  $R_2 = 0.038$ . The weighting scheme was as in I, and unobserved reflections were not included. The largest parameter shifts in the final cycle of refinement were less than 0.01 of their standard deviations. The estimated standard deviation of an observation of unit weight was 0.92. The final difference Fourier map showed no unaccounted electron density. The final values of positional and thermal parameters are given in Table 4. A tabulation of observed and calculated structure factor amplitudes is available for both compounds\*.

## Discussion

### A. Synthetic studies

The orange cyclopentadienyl complex,  $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2(\text{NO})$  (I), first reported by Fischer and coworkers [13], can be prepared by several methods: (a) Reaction of the dimer,  $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3]_2$ , with gaseous nitric oxide (in benzene) [13,14]; (b) Reaction of the salt,  $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3]\text{Na}$ , with *N*-methyl-*N*-nitroso-*p*-toluenesulphonamide ("diazald") (in diethyl ether) [15]; intermediate conversion of the anion into the hydride,  $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3\text{H}$ , by glacial acetic acid is widely used\*\* but appears not to be necessary [15]; (c) Reaction of the salt,  $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3]\text{Na}$ , with nitrosyl chloride, ClNO (in THF) [17]; (d) Reaction of arene tricarbonylchromium complexes,  $\text{ArCr}(\text{CO})_3$  (Ar = benzene or substituted benzene), with ClNO (below  $-30^\circ\text{C}$  in THF) and subsequent reaction of the solvent-stabilized intermediate,  $[\text{CrCl}(\text{CO})_2(\text{NO})] \cdot x \text{ THF}$ , with sodium cyclopentadienide (in THF) [8].

The nitrosylation by "diazald" (b) is the most convenient route. The direct combination of a  $[\text{Cr}(\text{CO})_2(\text{NO})]$  fragment with the cyclopentadienide ring (method d) has been extended to prepare the corresponding indenyl and fluorenyl complexes [8] (eq. 1).



(II)

The red-brown  $\eta^5\text{-9H}$ -fluorenyl complex,  $(\eta^5\text{-C}_{13}\text{H}_9)\text{Cr}(\text{CO})_2(\text{NO})$  (II) can be kept under inert gas at  $0^\circ\text{C}$ , but slowly disintegrates at ambient temperatures. Table 5 gives some characteristic spectroscopic data for the dicarbonylnitrosyl-

\* The tables of structure factors have been deposited as NAPS Document. Please contact ASIS/NAPS, c/o Microfiche Publications, 440 Park Avenue South, New York, N.Y. 10016.

\*\* The procedure is analogous to that described for  $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{NO})$  [16].

TABLE 5  
CHARACTERIZATION OF ANALOGOUS CYCLOPENTADIENYL AND FLUORENYL COMPLEXES

Complex	Color	Infrared		<sup>1</sup> H NMR <sup>a</sup>		
		$\nu(\text{CO})$ ( $\text{cm}^{-1}$ )	$\nu(\text{NO})$ ( $\text{cm}^{-1}$ )	$\delta(\text{C}_5\text{H}_5)$ (ppm)	$\delta(\text{H}(1)-\text{H}(8))$ (ppm)	$\delta(\text{H}(9))$ (ppm)
$(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2(\text{NO})$ (I)	orange	2028, 1959 <sup>b</sup>	1719 <sup>b</sup>	5.08	—	—
$(\eta^5\text{-C}_{13}\text{H}_9)\text{Cr}(\text{CO})_2(\text{NO})$ (II)	red-brown	2022 1955 <sup>b</sup>	1713 <sup>b</sup>	—	7.0-8.3(m)	5.81(s)
$(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$	yellow	2034 1949 <sup>c</sup>	—	4.80	—	—
$(\eta^5\text{-C}_{13}\text{H}_9)\text{Mn}(\text{CO})_3$ [18]	yellow-orange	2027 1944 <sup>c</sup>	—	—	7.2-8.0(m)	5.56(s)

<sup>a</sup>  $\text{CDCl}_3$  solution (rel. int. TMS). <sup>b</sup> n-Pentane solution (calibration by the polystyrene bands at 2850 and 1601  $\text{cm}^{-1}$ ). <sup>c</sup> Cyclohexane solution.



chromium compounds I and II, and for the isoelectric tricarbonylmanganese complexes,  $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$  and  $(\eta^5\text{-C}_{13}\text{H}_9)\text{Mn}(\text{CO})_3$  [18], respectively.

Although only a limited number of fluorenyl complexes is known [19], the bonding between the metal and the tricyclic ring system has been the subject of considerable discussion. Two X-ray structures have been reported which both indicate unexpected bonding situations. In the case of dichlorobis(fluorenyl)-zirconium,  $(\text{C}_{13}\text{H}_9)_2\text{ZrCl}_2$  [20], one of the two fluorenyl rings appears to be pushed out of its usual  $\eta^5$ -coordination to form a  $\pi$ -allylic-type  $\eta^3$ -bond. In the case of cyclopentadienyl(fluorenyl)iron,  $(\text{C}_5\text{H}_5)\text{Fe}(\text{C}_{13}\text{H}_9)$  [21,22], the metal is attached to a six-membered ring of the fluorenyl ligand which is no longer planar.  $\eta^6$ -Coordination is apparently typical for fluorenyl complexes which are formed by deprotonation of an  $\eta^6$ -fluorene ligand [21–24]. Two isomers are known of tricarbonyl(fluorenyl)manganese [21,23]: deprotonation of the  $[(\eta^6\text{-C}_{13}\text{H}_{10})\text{Mn}(\text{CO})_3]^+$  cation leads to the red  $(\eta^6\text{-C}_{13}\text{H}_9)\text{Mn}(\text{CO})_3$  [23], and this is irreversibly converted to the more stable, yellow-orange  $(\eta^5\text{-C}_{13}\text{H}_9)\text{Mn}(\text{CO})_3$  which had been directly prepared by the reaction of  $\text{Mn}(\text{CO})_5\text{Br}$  with sodium fluorenyl [18].

With respect to this versatility of the fluorenyl ligand, an X-ray investigation of  $(\text{C}_{13}\text{H}_9)\text{Cr}(\text{CO})_2(\text{NO})$  (II) appeared to be most desirable. The results described here afford a clear-cut case of  $\eta^5$ -coordination through the central five-membered ring.

It had been shown in earlier publications [25–27] that photolysis of  $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2(\text{NO})$  (I) in coordinating solvents (L) leads to substituted derivatives of the type  $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})(\text{NO})\text{L}$ . Although the analogous irradiation of  $(\eta^5\text{-C}_{13}\text{H}_9)\text{Cr}(\text{CO})_2(\text{NO})$  (II) in liquid olefins (L = cyclooctene, cycloocta-1,5-diene, norbornene, norbornadiene) or acetylenes (L = phenylacetylene) gave the expected fluorenyl compounds,  $(\eta^5\text{-C}_{13}\text{H}_9)\text{Cr}(\text{CO})(\text{NO})\text{L}$  (Table 1), these red complexes are much more labile in solution than their cyclopentadienyl counterparts. They are best characterized by their single  $\nu(\text{CO})$  and  $\nu(\text{NO})$  absorptions (Table 1). As in the cyclopentadienyl series, the  $\nu(\text{CO})$  frequency of the phenylacetylene complex  $(\eta^5\text{-C}_{13}\text{H}_9)\text{Cr}(\text{CO})(\text{NO})(\text{PhC}\equiv\text{CH})$  is higher by about  $30\text{ cm}^{-1}$  than that of the corresponding cycloolefin complexes, while the  $\nu(\text{NO})$  frequencies are nearly identical. The mononuclear cycloocta-1,5-diene complex tends to lose the olefin and is converted into a binuclear olefin-bridged compound,  $[(\eta^5\text{-C}_{13}\text{H}_9)\text{Cr}(\text{CO})(\text{NO})]_2\text{C}_8\text{H}_{12}$ , which is insoluble in pentane.

### B. X-ray studies

The molecular structure and atom numbering scheme for  $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2(\text{NO})$  (I) is shown in Fig. 1, and that of  $(\eta^5\text{-C}_{13}\text{H}_9)\text{Cr}(\text{CO})_2(\text{NO})$  (II) is given in Fig. 2. The structural parameters associated with the two compounds are quite similar in many respects, but there exist important differences. There is crystallographic disorder of the carbonyl and nitrosyl groups in the cyclopentadienyl compound, while no such difficulty was observed for the fluorenyl compound. The ordered structure for  $(\eta^5\text{-C}_{13}\text{H}_9)\text{Cr}(\text{CO})_2(\text{NO})$  (II) may be attributed to either steric or electronic effects. Evidence for a significant nonbonded interaction between the fused six-membered rings and the  $\text{X}=\text{O}$  groups may be seen from a comparison with  $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2(\text{NO})$  (I). For the fluorenyl derivative the Cr–centroid distance is longer (1.884 vs. 1.845 Å), the centroid–Cr–X

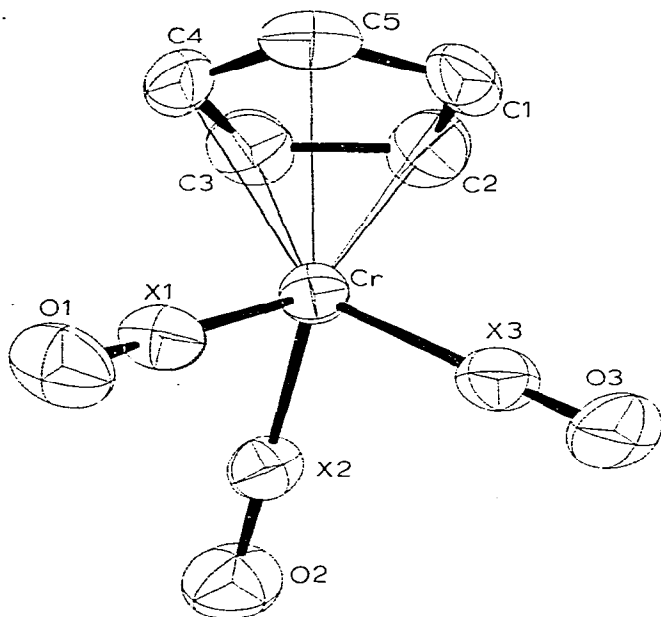


Fig. 1. Molecular structure of  $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2(\text{NO})$  (I) with the atoms represented by their 40% probability ellipsoids for thermal motion. One of the three disordered configurations is shown.

angles are larger ( $124.2^\circ$  vs.  $122.8^\circ$ ), and the X—Cr—X angles are smaller ( $91.8^\circ$  vs.  $93.3^\circ$ ). In addition, best planes calculations (Table 8) show that the plane of the five-membered ring is  $0.04 \text{ \AA}$  closer to the chromium atom than the plane based on the entire 13 carbon atom ligand. It must also be noted that the position of the nitrosyl is found where it would be expected from an electronic standpoint: the electron-withdrawing nitrosyl is “*trans*” to the electron-rich C(9) position.

The three independent Cr—C( $\pi$ ) bond lengths,  $2.183(8)$ ,  $2.248(5)$ , and  $2.270(5) \text{ \AA}$ , in  $(\eta^5\text{-C}_{13}\text{H}_9)\text{Cr}(\text{CO})_2(\text{NO})$  (II) show that the fluorenyl ligand is tilted to favor bonding to the C(9) position, but it is not possible to assess the relative contribution from steric and electronic effects. The shortest of the Cr—C( $\pi$ ) lengths favorably compares with the  $2.188(5) \text{ \AA}$  average found in  $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2(\text{NO})$  (I), and with the  $2.20(1) \text{ \AA}$  average value in  $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3]_2$  [28] and in  $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2\text{Cl}$  [2]. Although the fluorenyl group shows a spread of  $0.09 \text{ \AA}$  in metal—carbon distances, it must clearly be considered an  $\eta^5$ -ligand. In the compound regarded as  $(\eta^5\text{-C}_{13}\text{H}_9)(\eta^3\text{-C}_{13}\text{H}_9)\text{ZrCl}_2$  [20], the range of Zr—C( $\pi$ ) lengths for the  $\eta^5$ -ligand was  $0.25 \text{ \AA}$ .

In  $(\eta^5\text{-C}_{13}\text{H}_9)\text{Cr}(\text{CO})_2(\text{NO})$  (II) the Cr—N length,  $1.687(7) \text{ \AA}$ , falls in the range of reported values:  $1.63(1) \text{ \AA}$  in  $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})(\text{NMe}_2)]_2$  [5] to  $1.72(1) \text{ \AA}$  in  $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2(\text{NCO})$  [3]. The Cr—C (carbonyl) distance,  $1.864(6) \text{ \AA}$ , agrees well with the  $1.86 \text{ \AA}$  found in  $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3]_2$  [28]. The N≡O length of  $1.169(9) \text{ \AA}$  is larger than the C≡O distance of  $1.145(6) \text{ \AA}$ , in keeping with the

\* Average values used here are based on the individual values given in Tables 6 and 7.

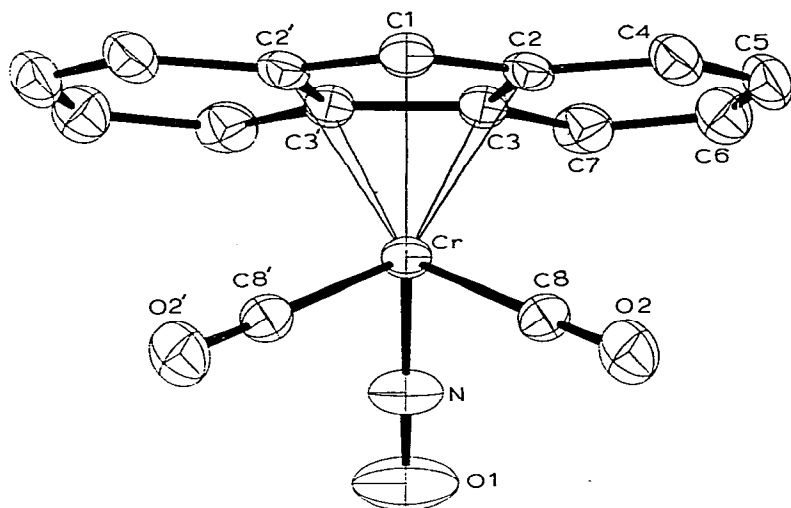


Fig. 2. Molecular structure of  $(\eta^5\text{-C}_{13}\text{H}_9)\text{Cr}(\text{CO})_2(\text{NO})$  (II).

greater antibonding population in the nitrosyl ligand. The  $\text{Cr-N-O}$  angle of  $178.9(7)^\circ$  is consistent with the  $\text{NO}^+$  formalism typical of linear  $\text{M-N-O}$  linkages, while the  $\text{Cr-C-O}$  angle of  $179.0(6)^\circ$  indicates the usual mode of bonding in the terminal metal carbonyl complexes.

The crystallographic disorder among the  $\text{X}\equiv\text{O}$  groups in  $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2(\text{NO})$  (I) has precluded an effective comparison of individual bond lengths. However, the average  $\text{Cr-X}$  distance, 1.801 Å, is essentially the same as that in  $(\eta^5\text{-C}_{13}\text{H}_9)\text{Cr}(\text{CO})_2(\text{NO})$  (II), 1.805 Å.

Stereoscopic views of the unit cell contents are shown in Fig. 3 and 4. No

TABLE 6

BOND LENGTHS (Å) AND ANGLES ( $^\circ$ ) FOR  $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2(\text{NO})$  (I)

Bond lengths (Å)			
Cr-C(1)	2.188(5)	X(1)-O(1)	1.160(5)
Cr-C(2)	2.187(5)	X(2)-O(2)	1.161(5)
Cr-C(3)	2.194(5)	X(3)-O(3)	1.142(5)
Cr-C(4)	2.184(5)	C(1)-C(2)	1.392(8)
Cr-C(5)	2.189(5)	C(2)-C(3)	1.387(7)
Cr-X(1)	1.812(5)	C(3)-C(4)	1.365(7)
Cr-X(2)	1.759(4)	C(4)-C(5)	1.398(8)
Cr-X(3)	1.831(4)	C(5)-C(1)	1.374(8)
Cr-Centroid	1.844		
Bond angles ( $^\circ$ )			
X(1)-Cr-X(2)	92.9(2)	X(2)-Cr-X(3)	93.6(2)
X(1)-Cr-X(3)	93.4(2)	X-Cr-Centroid	122.9
C(5)-C(1)-C(2)	109.8(5)	C(3)-C(4)-C(5)	109.4(5)
C(1)-C(2)-C(3)	106.6(5)	C(4)-C(5)-C(1)	105.9(5)
C(2)-C(3)-C(4)	108.3(5)	Cr-X(1)-O(1)	178.5(5)
Cr-X(2)-O(2)	178.7(4)	Cr-X(3)-O(3)	178.8(5)

TABLE 7

BOND LENGTHS (Å) AND ANGLES (°) FOR  $(\eta^5\text{-C}_{13}\text{H}_9)\text{Cr}(\text{CO})_2(\text{NO})$  (II)

Bond lengths (Å)			
Cr—C(1)	2.183(8)	C(1)—C(2)	1.429(7)
Cr—C(2)	2.248(5)	C(2)—C(3)	1.432(7)
Cr—C(3)	2.270(5)	C(3)—C(3') <sup>a</sup>	1.443(10)
Cr—N	1.687(7)	C(2)—C(4)	1.440(7)
Cr—C(8)	1.864(6)	C(4)—C(5)	1.362(9)
N—O(1)	1.169(9)	C(5)—C(6)	1.411(10)
C(8)—O(2)	1.145(6)	C(6)—C(7)	1.377(8)
Cr—Centroid	1.884	C(7)—C(3)	1.422(7)
Bond angles (°)			
N—Cr—C(8)	95.3(3)	C(1)—C(2)—C(4)	131.5(6)
C(8)—Cr—C(8')	88.4(3)	C(3)—C(2)—C(4)	119.3(5)
Cr—N—O(1)	178.9(7)	C(2)—C(4)—C(5)	117.7(6)
Cr—C(8)—O(2)	179.0(6)	C(4)—C(5)—C(6)	123.0(5)
N—Cr—Centroid	128.5	C(5)—C(6)—C(7)	121.1(6)
C(8)—Cr—Centroid	119.9	C(6)—C(7)—C(3)	118.1(6)
C(2)—C(1)—C(2')	106.8(7)	C(7)—C(3)—C(2)	120.7(5)
C(1)—C(2)—C(3)	109.1(5)	C(7)—C(3)—C(3')	131.9(3)
C(2)—C(3)—C(3')	107.3(3)		

<sup>a</sup> Primed atoms are related to those given in Table 3 by  $(x, \frac{1}{2}-y, z)$ .

TABLE 8

LEAST-SQUARES PLANES FOR  $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2(\text{NO})$  AND  $(\eta^5\text{-C}_{13}\text{H}_9)\text{Cr}(\text{CO})_2(\text{NO})$ 

Plane <sup>a</sup>					
A	$-0.6161X - 0.7849Y - 0.0666Z - 0.3493 = 0$				
B	$0.2990X + 0.0000Y - 0.9543Z - 1.6948 = 0$				
C	$0.3037X + 0.0000Y - 0.9528Z - 1.7515 = 0$				
Deviation of atoms from planes (Å)					
Atom	Plane A	Atom	Plane B	Atom	Plane C
C(1)	0.010	C(1)	-0.032	C(1)	-0.072
C(2)	-0.009	C(2)	0.026	C(2)	-0.020
C(3)	0.006	C(3)	-0.010	C(3)	-0.061
C(4)	0.000	C(2')	0.026	C(4)	0.038
C(5)	-0.006	C(3')	-0.010	C(5)	0.066
Cr	-1.844	Cr	-1.883	C(6)	0.039
				C(7)	-0.028
				C(2')	-0.020
				C(3')	-0.061
				C(4')	0.038
				C(5')	0.066
				C(6')	0.039
				C(7')	-0.028
				Cr	1.928

<sup>a</sup> Plane A corresponds to the plane of the cyclopentadienyl group in  $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2(\text{NO})$ . Plane B and C relate to  $(\eta^5\text{-C}_{13}\text{H}_9)\text{Cr}(\text{CO})_2(\text{NO})$ .

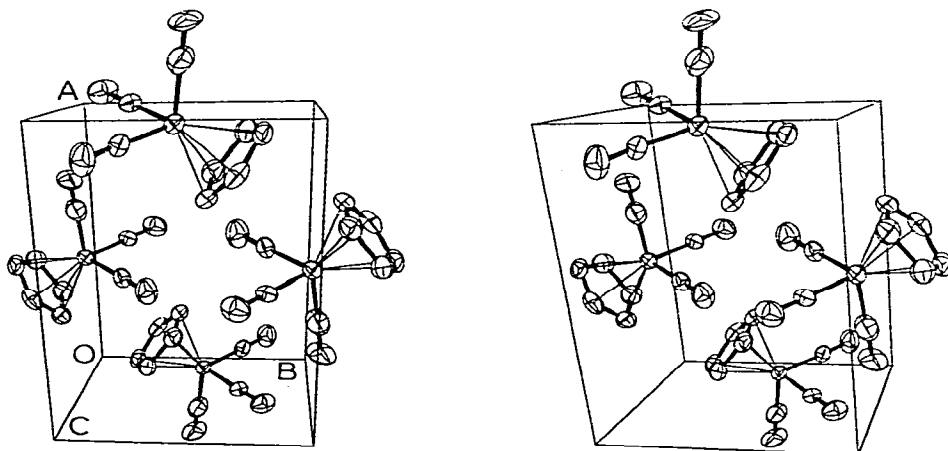


Fig. 3. Stereoscopic view of the unit cell packing of I.

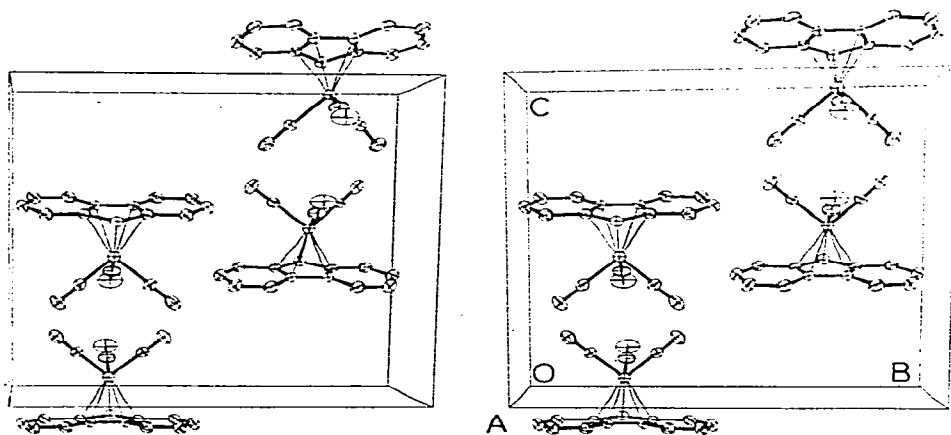


Fig. 4. Stereoscopic view of the cell packing of II.

unusually close intermolecular contacts are revealed, but the two molecules pack in a distinctly different fashion. In  $(\eta^5\text{-C}_{13}\text{H}_9)\text{Cr}(\text{CO})_2(\text{NO})$  the fluorenyl ligands on adjacent molecules are near-neighbors, while the  $(\text{XO})_3$  tripods are stacked in an interlocking manner. Such is not the case for  $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2(\text{NO})$ .

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