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# Preparation and Structure of ($\mu$-Phenanthrene)- and ($\mu$-Pyrene)bis(tricarbonylchromium)

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The preparations of the bis(tricarbonylchromium) complexes of phenanthrene and pyrene are reported. These materials were characterized by spectroscopic means, including both their solution and solid CP/MAS NMR spectra. The X-ray crystal structure showed both complexes to have the anticipated anti orientation of the tricarbonylchromium moieties. In the phenanthrene complex, the rotomer conformations for the two tricarbonylchromium groups are different, whereas the pyrene complex has a center of inversion.

## Introduction

Tricarbonylchromium(0) ($Cr(CO)_3$) polycyclic aromatic hydrocarbon (PAHs) complexes have interesting and useful properties ranging from hydrogenation catalysis[1] to arene activation.[2] Many PAH mono(tricarbonylchromium) complexes are known.[3] The regiochemical control for preference of terminal ring complexation in cata condensed PAHs has been explained on the basis of simple localization energy arguments. This rationale correctly predicts the regiochemistry in the known complexes but also suggests that the introduction of a second tricarbonylchromium moiety should be difficult. Except for the examples given below for chromium, this expectation has been borne out by experiment.

There are many (arene)$(Cr(CO)_3)_2$ complexes known.[4–16] Frequently, such complexes have conjugatively insulating groups between the complexed rings like 9,10-dihydroanthracene[4] or longer carbon[5] or ether[6] chains. Others bear intervening heteroatoms such as phosphorus or mercury.[8] Most of those having formal conjugation involve relatively flexible structures such as biphenyl[9–11], phenylanthracene,[12] triphenylbenzene,[13] or other flexible groups[7,14,16] where the two complexed rings are nonplanar and may have little conjugative interaction. A few examples of rigid systems which have the possibility of conjugation between the rings or of steric interaction between the two tricarbonylchromium groups have been observed.[17,18] Notable among these are the fluorene anion bis complex,[17a] the dinaphthofuran bis complex,[18a] and the 9,10-dihydrophenanthrene bis complex.[18b] PAHs which form rigid bis(tricarbonylchromium) complexes are fluorene,[17b] triphenylene,[18c] azulene,[18d] and starphenylene.[18e] The fluorene complex has been shown by NMR to have anti orientation of the tricarbonylchromium moieties. The triphenylene and starphenylene complexes were assumed anti on steric grounds. The azulene complex, however, was different (note that no naphthalene bis(tricarbonylchromium) complex is known) because the tricarbonylchromium moieties are syn with the chromium atoms within bonding distance, as determined by X-ray crystallographic analysis.

We now wish to report the ready formation of the bis(tricarbonylchromium) complexes of phenanthrene ($C_{14}H_{10}$)(phen) and pyrene ($C_{16}H_{10}$)(pyr) and their X-ray crystallographic structure determinations. Recent reports of the bis(hexamethylbenzene–ruthenium)[19] and the bis(iron)[20] complexes of PAHs and those reported above indicate that the bis form of complexation is probably general although it has not been studied or utilized extensively.

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## Experimental Section

All solvents were dried and degassed. All manipulations were carried out under nitrogen or in a vacuum using Schlenk line or glovebox techniques where necessary. Phenanthrene was recrystallized from methanol, and pyrene, from toluene. Melting points (vacuum sealed capillary using a Mel-Temp apparatus) are uncorrected. IR spectra were determined on a KBr mixture by diffuse reflectance on a Bio-Rad FTS-40 spectrometer. NMR spectra both solution and solid CP/MAS were determined on a Varian VXR 300 and recorded in ppm vs TMS.

**($\mu$-Phenanthrene)bis(tricarbonylchromium) (1).** Phenanthrene (0.16 g, 0.89 mmol) and $(NH_3)_3(Cr(CO)_3)$ (0.50 g, 2.7 mmol)[21] were added to anhydrous diethyl ether (20 mL) with magnetic stirring. Then boron trifluoride etherate (1.66 mL) was slowly syringed into the mixture. After stirring for 48 h the reaction mixture was diluted with methylene chloride and washed with 1 M HCl solution. The organic layer was distilled and the residue dried under vacuum, then placed on a dry pack silica chromatography column, and developed with petroleum ether (bp 40–60 °C). The product (1) was removed with 1:1 petroleum ether:chloroform. Yield: 0.195 g (49%). Both phenanthrene and the mono(tricarbonylchromium) (phenanthrene) complex were removed in the forerun. Mp: 222 °C dec. IR: 1970.7, 1902.7, 1893.9 cm$^{-1}$. $^1$H NMR: see Table I. $^{13}$C NMR ($CDCl_3$): $\delta$ 84.9 ($C_4$), 91.6 ($C_3$), 91.7 ($C_2$), 98.1 ($C_1$), 98.9 ($C_{8a}$), 100.7 ($C_{4a}$), 128.7 ($C_9$), 231.4 (CO). $^{13}$C NMR (CP/MAS solids): $\delta$ 85.7 ($C_{4,5}$), 93.9 and 95.4 ($C_{1,2,3,6,7,8}$), 99.2 ($C_{8a,10a}$), 105.9 and 107.6 ($C_{4a,4b}$), 127.7 and 134.0 ($C_{9,10}$), 233–237 (br, CO). HRMS: calcd for $C_{20}H_{10}{}^{52}Cr_2O_6$ 449.9288, found (EI) 449.9289; calcd for $C_{20}H_{10}{}^{53}Cr^{52}CrO_6$ 450.9289, found 450.9308.

**($\mu$-Pyrene)bis(tricarbonylchromium) (2).** To pyrene (0.104 g, 0.514 mmol) and $(NH_3)_3(Cr(CO)_3)$ (0.48 g, 2.5 mmol)[21] in a stirred anhydrous diethyl ether (20 mL) solution was slowly syringed in boron trifluoride etherate solution (1.58 mL). After 3 days the mixture was diluted with methylene chloride and washed with 1 M HCl solution. The organic layer was evaporated under vacuum, and the products were separated using dry pack chromatography on silica gel with petroleum ether (bp 40–60 °C) followed by a 1:1 petroleum ether:chloroform mixture to yield 0.112 g (46%) of 2. Mp: 209 °C dec. IR: 1938.8, 1863.5, 1827.1 cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 5.460 (t, 2H, $J_{12} = 6.45$ Hz, $H_2$), 5.801 (d, 4H, $H_1$), 7.232 (s, 4H, $H_4$). $^{13}$C NMR (acetone-$d_6$): $\delta$ 93.1 ($C_{1,3}$), 94.1 ($C_2$), 129.9 ($C_4$), 233.4 (CO). $^{13}$C NMR (CP/MAS solids): $\delta$ 84.4, 93.3, 100.8 ($C_{1,2,3a,10b}$); 125.8 ($C_4$); 227.6, 230.4, 232.4 (CO). HRMS: calcd for $C_{22}H_{10}{}^{52}Cr_2O_6$ 473.9288, found (EI) 473.9278.

**X-ray Structural Determination of $(Cr(CO)_3)_2$(phen) (1).** A red single crystal of 1 was cut and mounted on a glass fiber using silicon adhesive with the longest dimension parallel to the fiber. The lattice was examined and data were collected with a Picker four circle diffractometer fitted with a Crystal Logic automation package.[22] A triclinic unit cell was selected and verified by Laue photographs.

Intensity data were collected using a 1-mil zirconium filter. The intensities of three standard reflections, taken every 97 measurements, varied an average of 1.1%, and consequently, no decay correction was necessary. Four large reflections (020, 1,–2,1, 101, 1,2,–1) had intensities greater than the maximum allowable count rate for the detector. These were recollected at reduced tube power and given a separate scale factor during refinement. Relevant crystal data are given in Table II.

**Table I. $^1$H NMR of ($\mu$-Phenanthrene)bis(tricarbonylchromium)**

| | | chem shift, ppm | | coupling const, Hz | |
|---|---|---|---|---|---|
| assgnt[a] | mult | found | calcd[b] | found | calcd[b] |
| C2 | d of t | 5.529 | 5.528 | $J_{1,2} = 6.24$ | 6.40 |
| C3 | d of t | 5.572 | 5.567 | $J_{1,3} = 1.41$ | 1.20 |
| C1 | dd | 5.872 | 5.855 | $J_{1,4} = 0$ | 0.02 |
| C4 | dd | 6.223 | 6.220 | $J_{2,3} = 6.1$ | 5.89 |
| C9 | s | 7.185 | | $J_{2,4} = 0.98$ | 1.00 |
| | | | | $J_{3,4} = 6.53$ | 6.68 |

[a] Assignments were made by COSY and decoupling experiments and by analogy to the (phenanthrene)(tricarbonylchromium) spectrum.[2b] [b] Spectra were simulated by the Varian VXR-300 version of the SPINS program.

**Table II. Crystal Data**

| | $(Cr(CO)_3)_2$(phen) (**1**) | $(Cr(CO)_3)_2$(pyr) (**2**) |
|---|---|---|
| fw | 450.29 | 474.31 |
| space group | $P\bar{1}$ | $P\bar{1}$ |
| cryst dimens, mm | 0.13 × 0.20 × 0.43 | 0.17 × 0.20 × 0.30 |
| cryst color | pale red | burgundy |
| cryst habit | rhombus rt prism | rhombus rt prism |
| $a$, Å | 10.344(1) | 6.583(1) |
| $b$, Å | 13.473(2) | 8.416(1) |
| $c$, Å | 6.810(1) | 13.501(2) |
| $\alpha$, deg | 102.342(4) | 79.402(4) |
| $\beta$, deg | 80.299(4) | 44.903(1) |
| $\gamma$, deg | 107.933(3) | 61.300(3) |
| $Z$ | 2 | 1 |
| $V$, Å$^3$ | 876.71 | 448.16 |
| $\rho$(calcd), g cm$^{-3}$ | 1.71 | 1.76 |
| radiation ($\lambda$), Mo K$\alpha$ | 0.7107 | 0.7107 |
| abs coeff ($\mu$), cm$^{-1}$ | 12.44 | 12.22 |
| transm factor range | 0.91–0.76 | 0.84–0.78 |
| $F$(000), e | 452 | 238 |
| temp, K | 296 | 294 |
| scan mode; speed, deg/min | $\theta$–$2\theta$; 3.0 | $\theta$–$2\theta$; 3.0 |
| $2\theta$ range, deg | 1–50.67 | 1–63.7 |
| no. of unique data collcd | 3212 | 3075 |
| no. of unique data obsd | 2741 ($I > 3\sigma(I)$) | 2636 ($I > 3\sigma(I)$) |
| no. of parms refined | 254 | 137 |
| final shift/error, max and av | 0.013, 0.001 | 0.020, 0.002 |
| final diff map, max and min, Å$^3$ | 0.67–0.54 | 2.32–2.81 |
| $R = \sum\lVert F_o\rvert - \lvert F_c\rVert/\sum\lvert F_o\rvert$ | 0.028 | 0.030 |
| $R_w = (\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2)^{1/2}$ | 0.043 | 0.049 |

Direct methods[22] were used to locate all non-hydrogen atoms in the asymmetric unit of the structure. Full matrix isotropic refinement of all non-hydrogen atoms ($R = 0.079$, $R_w = 0.112$) was followed by fully anisotropic refinement which converged with $R = 0.042$ and $R_w = 0.066$. Absorption corrections, calculated from average path lengths,[22] were then applied to the data and further refinement reduced $R$ to 0.038 and $R_w$ to 0.063. Coordinates for the hydrogen atoms on the phenanthrene ring were calculated assuming a 0.95-Å distance from their corresponding carbon atoms and included as fixed contributors in the final refinement which converged with $R = 0.028$, $R_w = 0.043$, and GOF = 1.69. Atomic coordinates from the final refinement are listed in Table III.

**X-ray Structure Determination of $(Cr(CO)_3)_2$(pyr) (2).** The structure determination of 2 was carried out in a manner analogous to that of 1. Because the intensity of the standard reflections showed an average decay of only 0.6% over 57.1 h of exposure, no decay correction was necessary. Three reflections (0,1,–1, 010, 111) had intensities greater than the maximum allowed count rate of the detector and were recollected at reduced tube power and given a separate scale factor in refinement.

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(22) The Crystal Logic package includes modified versions of the following programs: REDUCE (Broach, Coppens, Becker, and Blessing), peak profile analysis, Lorentz and polarization corrections; ORFLS (Busing, Martin, and Levy), structure factor calculation and full-matrix least squares refinement; ORFFE (Busing, Martin, and Levy), distance angle and error calculations; ABSORB (Coppens, Edwards, and Hamilton), absorption correction calculation; ORTEP (Johnson), figure plotting; HYDROGEN (Trueblood), calculation of hydrogen atomic positions; and SHELLX-86 (Sheldrick), direct methods. All calculations were preformed on a DEC Microvax 3100 computer. Scattering factors and corrections for anomalous dispersion were taken from: *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

**Table III. Positions and Equivalent Isotropic Temperature Factors for $(Cr(CO)_3)_2(phen)$ (1)**

| atom | $x$ | $y$ | $z$ | $10^4U_{eq}{}^a$ |
|---|---|---|---|---|
| Cr(1) | −0.49783(4) | 0.20848(3) | 0.38309(5) | 296(3) |
| Cr(2) | 0.02705(4) | 0.26126(3) | −0.00444(5) | 265(3) |
| C(1) | −0.3652(3) | 0.3415(2) | 0.5720(4) | 392(21) |
| C(2) | −0.4076(3) | 0.2560(2) | 0.6736(4) | 429(22) |
| C(3) | −0.3865(3) | 0.1576(2) | 0.5751(4) | 401(22) |
| C(4) | −0.3218(2) | 0.1462(2) | 0.3782(4) | 339(19) |
| C(4a) | −0.2727(2) | 0.2344(2) | 0.2731(4) | 289(17) |
| C(4b) | −0.1993(2) | 0.2269(2) | 0.0688(3) | 280(17) |
| C(5) | −0.1658(2) | 0.1335(2) | −0.0355(4) | 344(19) |
| C(6) | −0.0875(3) | 0.1314(2) | −0.2266(4) | 399(21) |
| C(7) | −0.0383(3) | 0.2225(2) | −0.3133(4) | 420(22) |
| C(8) | −0.0709(3) | 0.3165(2) | −0.2141(4) | 377(21) |
| C(8a) | −0.1510(2) | 0.3195(2) | −0.0256(4) | 314(18) |
| C(9) | −0.1852(3) | 0.4160(2) | 0.0796(4) | 372(20) |
| C(10) | −0.2536(3) | 0.4214(2) | 0.2644(4) | 374(20) |
| C(10a) | −0.2959(2) | 0.3330(2) | 0.3714(4) | 322(19) |
| C(15) | −0.5866(3) | 0.3017(2) | 0.3467(5) | 465(24) |
| C(16) | −0.6618(3) | 0.1304(2) | 0.5017(4) | 404(22) |
| C(17) | −0.5449(2) | 0.1297(2) | 0.1354(4) | 371(21) |
| C(18) | 0.0882(3) | 0.1716(2) | 0.1019(4) | 425(22) |
| C(19) | 0.2063(3) | 0.3183(2) | −0.1079(4) | 405(22) |
| C(20) | 0.0635(2) | 0.3611(2) | 0.2253(4) | 328(19) |
| O(1) | −0.6408(3) | 0.3615(2) | 0.3283(5) | 810(28) |
| O(2) | −0.7624(2) | 0.0823(2) | 0.5750(3) | 625(21) |
| O(3) | −0.5758(2) | 0.0823(2) | −0.0201(3) | 565(19) |
| O(4) | 0.1252(3) | 0.1153(2) | 0.1688(4) | 739(25) |
| O(5) | 0.3177(2) | 0.3558(2) | −0.1641(4) | 669(22) |
| O(6) | 0.0847(2) | 0.4245(2) | 0.3682(3) | 551(19) |

[a] $U_{eq} = [1/(6\pi^2)]\sum\sum\beta_{ij}a_ia_j$.

**Table IV. Positions and Equivalent Isotropic Temperature Factors (Å²) for $(Cr(CO)_3)_2(pyr)$ (2)**

| atom | $x$ | $y$ | $z$ | $10^4U_{eq}{}^a$ |
|---|---|---|---|---|
| Cr(1) | 0.23770(1) | 0.13320(4) | 0.25278(3) | 262(5) |
| C(1) | −0.0896(5) | 0.0337(3) | 0.3236(2) | 346(31) |
| C(2) | −0.2692(4) | 0.2300(3) | 0.3675(2) | 376(31) |
| C(3) | −0.1469(4) | 0.3368(3) | 0.2679(2) | 347(30) |
| C(3a) | 0.1613(4) | 0.2467(2) | 0.1206(2) | 285(28) |
| C(9) | 0.7013(5) | −0.3504(2) | −0.0139(2) | 329(32) |
| C(10) | 0.4132(5) | −0.2634(3) | 0.1261(2) | 343(34) |
| C(10a) | 0.2195(4) | −0.0600(2) | 0.1765(2) | 285(28) |
| C(10b) | 0.3434(4) | 0.0466(2) | 0.0747(2) | 253(26) |
| C(11) | 0.5632(5) | 0.1988(3) | 0.1531(2) | 364(36) |
| C(12) | 0.0479(5) | 0.2607(3) | 0.4292(2) | 355(31) |
| C(13) | 0.4962(5) | −0.0718(3) | 0.2750(2) | 337(32) |
| O(11) | 0.7647(5) | 0.2376(3) | 0.0820(2) | 596(45) |
| O(12) | −0.0635(5) | 0.3360(2) | 0.5329(2) | 540(35) |
| O(13) | 0.6589(4) | −0.1982(2) | 0.2848(2) | 516(37) |

[a] $U_{eq} = [1/(6\pi^2)]\sum\sum\beta_{ij}a_ia_j$.

The experimental density of 1.766(1) g/cm³ was determined by floatation in a zinc bromide solution. The structure determination was accomplished using Patterson and Fourier techniques. Full matrix isotropic refinement produced $R = 0.064$ and $R_w = 0.094$, and anisotropic refinement produced $R = 0.038$ and $R_w = 0.062$. Average path length absorption corrections were applied to the data, and refinement converged at $R = 0.038$, $R_w = 0.063$. Theoretical hydrogen atoms were then included in the final refinement which converged with $R = 0.030$, $R_w = 0.049$, and GOF = 1.73. Atomic coordinates from the final refinement are listed in Table IV.

Although final refinement converged smoothly, several atoms in 2 had high correlations (in the range 0.80–0.95) between their individual anisotropic thermal parameters ($\beta_{13}$ to $\beta_{11}$ and $\beta_{33}$). In addition, the largest (2.32 e/Å³) and smallest (−2.81 e/Å³) residual electron densities were in the vicinity of O(9), which may represent some orientational disorder of the CO groups. Several residuals on the order of 1.5 e/Å³ were also observed near the hydrogen positions. No consistent model for a general orientational disorder of the CO groups was obvious, however.

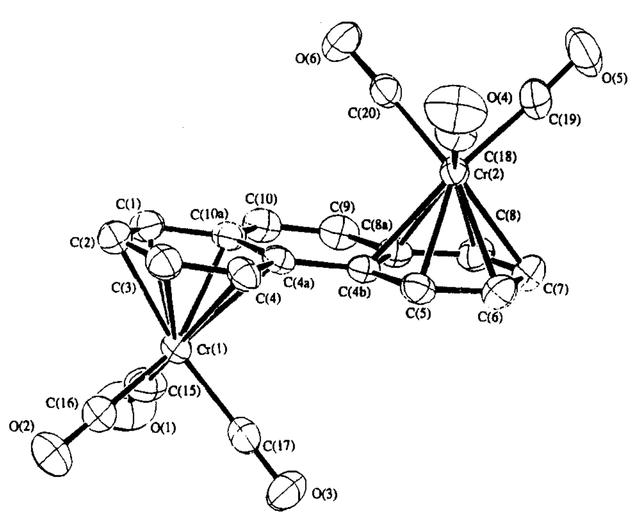

**Figure 1.** ORTEP diagram of one molecule of 1 depicting the atomic numbering scheme and thermal ellipsoids at 50% probabililty.

## Results and Discussion

In the thermal preparation of the mono(tricarbonylchromium) complex of phenanthrene (from $Cr(CO)_6$ and phenanthrene) if the reaction time was prolonged or if a more active chromium reagent was used, the presence of a second product was evident by tlc. Thus, refluxing a 10:1 dibutyl ether:THF solution of phenanthrene and chromium hexacarbonyl for 4 or 5 days (compared to the 15 h used in the mono complex[3] preparation) or the use of tris(ammonia)tricarbonylchromium[21] with phenanthrene in refluxing dioxane allowed formation of two products. The best yields were obtained by use of the latter reagents in excess, potentiated with boron trifluoride etherate at room temperature (see Experimental Section). The products were separated by chromatography. The less polar compound proved to be the mono(tricarbonylchromium)(phenanthrene). The ¹H NMR spectrum (Table I) of the more polar compound showed only one proton downfield (δ 7.18 ppm) with all other protons in positions typical of chromium tricarbonyl complexed aryl rings (δ 5.5–6.2 ppm). The symmetry of the spectrum confirmed the structural assignment. Two questions remained. Were the $Cr(CO)_3$ moieties anti as anticipated? What was the conformation of the $Cr(CO)_3$ groups relative to the complexed rings? X-ray structure determinations were carried out to answer these questions for both complexes.

**Structure of $(Cr(CO)_3)_2(phen)$ (1).** An ORTEP diagram of one molecule of 1 is depicted in Figure 1. The $Cr(CO)_3$ moieties are both π-bonded to opposite faces of the two terminal rings in the phenanthrene ligand. The projection of the carbonyls onto the plane of the phenanthrene in Figure 2 shows that both $Cr(CO)_3$ groups are closer to being staggered then eclipsed with respect to the ring carbon atoms and are approximately 60° out of phase with one another. The conformation of the first $Cr(CO)_3$ moiety, at Cr(1), is exo (two carbonyls skewed relative to the adjacent ring) while the second $Cr(CO)_3)$ is endo (with one carbonyl over the adjacent ring)[18c]. Bond distances and angles are listed in Tables V and VI, respectively.

The chromium atoms occupy anti (sterically less hindered) positions with respect to the phenanthrene plane. An example of syn coordination has been previously

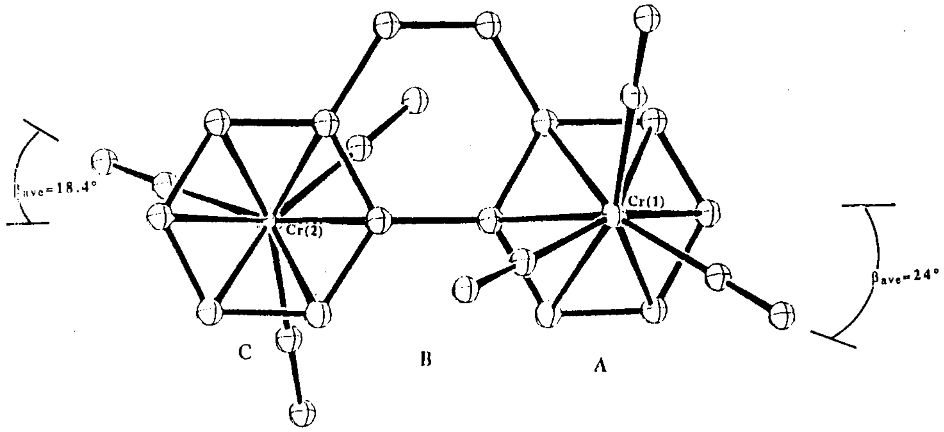

**Figure 2.** Projection of the two Cr(CO)$_3$ moieties of 1 onto the phenanthrene plane. The angle β is the average rotation angle between the CrCtCO planes and the CCtCrC ring plane where Ct is the ring center.

**Table V. Interatomic Distances (Å) for (Cr(CO)$_3$)$_2$(phen) (1)**

| | | | |
|---|---|---|---|
| Cr(1)–C(15) | 1.844(3) | C(2)–C(3) | 1.416(4) |
| Cr(1)–C(17) | 1.845(3) | C(3)–C(4) | 1.394(4) |
| Cr(1)–C(16) | 1.855(3) | C(4)–C(4a) | 1.432(3) |
| Cr(1)–C(1) | 2.201(3) | C(4a)–C(10a) | 1.426(3) |
| Cr(1)–C(3) | 2.210(2) | C(4a)–C(4b) | 1.467(3) |
| Cr(1)–C(2) | 2.216(3) | C(4b)–C(5) | 1.418(3) |
| Cr(1)–C(4) | 2.220(2) | C(4b)–C(8a) | 1.439(3) |
| Cr(1)–C(10a) | 2.242(2) | C(5)–C(6) | 1.412(4) |
| Cr(1)–C(4a) | 2.265(2) | C(6)–C(7) | 1.392(4) |
| Cr(2)–C(18) | 1.839(3) | C(7)–C(8) | 1.412(4) |
| Cr(2)–C(20) | 1.840(3) | C(8)–C(8a) | 1.406(4) |
| Cr(2)–C(19) | 1.854(3) | C(8a)–C(9) | 1.459(3) |
| Cr(2)–C(5) | 2.205(2) | C(9)–C(10) | 1.335(4) |
| Cr(2)–C(7) | 2.224(3) | C(10)–C(10a) | 1.444(4) |
| Cr(2)–C(6) | 2.225(3) | C(15)–O(1) | 1.151(4) |
| Cr(2)–C(4b) | 2.233(2) | C(16)–O(2) | 1.140(3) |
| Cr(2)–C(8) | 2.241(2) | C(17)–O(3) | 1.153(3) |
| Cr(2)–C(8a) | 2.249(2) | C(18)–O(4) | 1.147(3) |
| C(1)–C(2) | 1.388(4) | C(19)–O(5) | 1.142(3) |
| C(1)–C(10a) | 1.430(4) | C(20)–O(6) | 1.152(3) |

**Table VI. Bond Angles (deg) for (Cr(CO)$_3$)$_2$(phen) (1)**

| | | | |
|---|---|---|---|
| C(15)–Cr(1)–C(17) | 88.35(12) | C(7)–C(6)–C(5) | 120.25(24) |
| C(15)–Cr(1)–C(16) | 88.85(13) | C(6)–C(7)–C(8) | 120.10(24) |
| C(17)–Cr(1)–C(16) | 88.52(11) | C(8a)–C(8)–C(7) | 120.42(23) |
| C(18)–Cr(2)–C(20) | 89.45(12) | C(8)–C(8a)–C(4b) | 120.14(22) |
| C(18)–Cr(2)–C(19) | 87.92(12) | C(8)–C(8a)–C(9) | 121.18(22) |
| C(20)–Cr(2)–C(19) | 87.28(11) | C(4b)–C(8a)–C(9) | 118.67(22) |
| C(2)–C(1)–C(10a) | 121.05(24) | C(10)–C(9)–C(8a) | 121.46(23) |
| C(1)–C(2)–C(3) | 119.63(24) | C(9)–C(10)–C(10a) | 121.95(23) |
| C(4)–C(3)–C(2) | 120.65(24) | C(4a)–C(10a)–C(1) | 119.37(23) |
| C(3)–C(4)–C(4a) | 120.66(24) | C(4a)–C(10a)–C(10) | 119.49(22) |
| C(10a)–C(4a)–C(4) | 118.57(23) | C(1)–C(10a)–C(10) | 121.10(23) |
| C(10a)–C(4a)–C(4b) | 119.02(22) | O(1)–C(15)–Cr(1) | 178.30(27) |
| C(4)–C(4a)–C(4b) | 122.41(22) | O(2)–C(16)–Cr(1) | 179.78(25) |
| C(5)–C(4b)–C(8a) | 118.07(21) | O(3)–C(17)–Cr(1) | 178.30(24) |
| C(5)–C(4b)–C(4a) | 122.63(21) | O(4)–C(18)–Cr(2) | 179.43(27) |
| C(8a)–C(4b)–C(4a) | 119.17(21) | O(5)–C(19)–Cr(2) | 177.25(25) |
| C(6)–C(5)–C(4b) | 120.98(23) | O(6)–C(20)–Cr(2) | 178.73(22) |

reported in the tris complex (Re(CO)$_3$)$_3$(trindenyl).[23] Both chromium atoms are shifted slightly from the aromatic ring centers, by 0.031 Å for Cr(1) and 0.026 Å for Cr(2), toward the ring ends. Both chromium atoms have octahedral geometry, if the midpoints of the double bonds trans to the carbonyls are counted as individual ligands. An average carbonyl C–Cr–C angle of 88.4(1)° then results. The two Cr to ring distances of 1.718 and 1.724 Å for Cr(1) and Cr(2), respectively, are similar, and the average distance is 1.721 Å. Rings A and C are planar (within 0.013 Å); however, they have approximately a 3° steplike fold from the mean plane of central ring B.

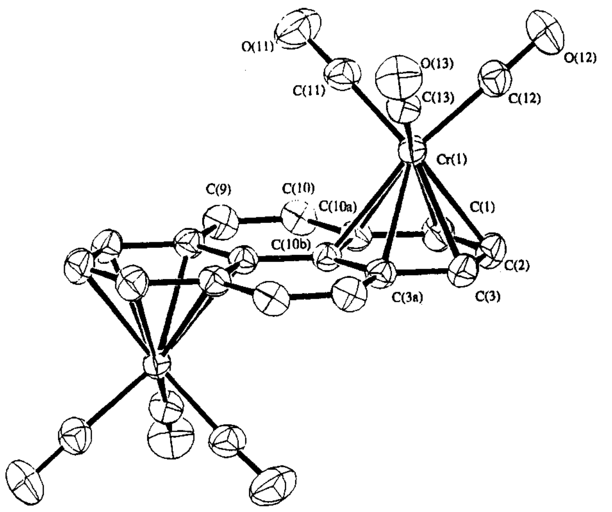

**Figure 3.** ORTEP diagram of one molecule of 2 depicting the atomic numbering scheme for the asymmetric unit of structure and thermal ellipsoids at 50% probability. The numbering for the asymmetric unit of the structure follows the organic convention. Using prime notation to denote those atoms related by the center of inversion, conventional numbering for the other half of the molecule can be derived as follows: Cr(1)′ = Cr(2), C(9)′ = (C4), C(10)′ = C(5), C(10a)′ = C(5a), C(1)′ = C(6), C(2)′ = C(7), C(3)′ = C(8), C(3a)′ = C(8a), C(10b)′ = C(10c), C(11)′ = C(14), C(12)′ = C(15), C(13)′ = C(16), O(11)′ = O(14), O(12)′ = O(15), O(13)′ = O(16).

Carbon–carbon bond distances in (Cr(CO)$_3$)$_2$(phen) show interesting changes compared to the previously uncomplexed ring in the monocoordinated ligand. The observed C(7)–C(8) bond of 1.412(4) Å is about 0.05 Å longer than that reported in the monocoordinated (Cr(CO)$_3$)(phen)[24,25] or the free phenanthrene.[26] The observed C(4b)–C(8a) and C(8a)–C(9) distances also appear to be slightly longer by 0.03 Å upon bis complexation. Given the fact that the C(7)–C(8) bond length in mono (Cr(CO)$_3$)(phen) is 1.35(1) Å,[3] it is somewhat surprising that the second Cr(CO)$_3$ in the bis complex does not take advantage of the localized electron density in this bond. If it did, the orientation of the Cr(CO)$_3$ groups would need to rotate

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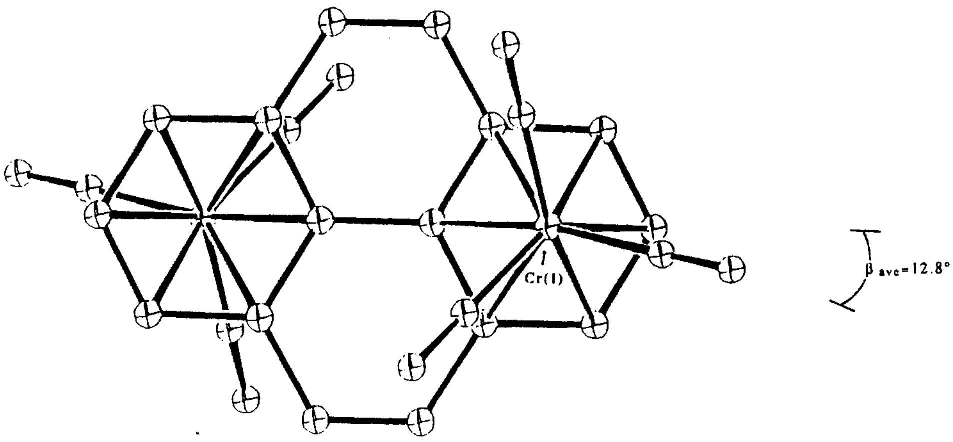

**Figure 4.** Projection of the two $Cr(CO)_3$ moieties in **2** onto the pyrene plane. The angle β is the rotation angle between the CrCtCO plane and the CCtCrC ring plane where Ct is the ring center.

approximately 30°, assuming an octahedral arrangement of orbitals on Cr.

In view of the previously determined preference for the exo conformation of the $Cr(CO)_3$ group[18c] in mono complexes, a rationale was sought for the presence of both the exo and endo conformations for the $Cr(CO)_3$ groups of **1**. Currently, no assessment of the possibility of intramolecular electronic factors in favoring this conformation can be made. However, intermolecular steric factors do appear to be important. In an attempt to check packing forces, theoretical coordinates for the three carbonyl groups on Cr(2) were calculated for 10° incremental rotations about the Cr(2) to ring center axis.[22] These results show that the observed rotation angle of 18° represents a minimum and rotations of over 30° and under 10° place portions of $Cr(CO)_3$ closer than a normal van der Waals radii distance to atoms in neighboring phenanthrene ligands. It appears, therefore, that packing forces alone could be responsible for forcing both exo and endo conformations on the bis complex **1**.

**Structure of $(Cr(CO)_3)_2(pyr)$ (2).** An ORTEP diagram of one molecule of **2** is depicted in Figure 3. The molecule resides on a crystallographic center of inversion that occurs at the midpoint of the C(10b)–C(10b)′ bond where the prime notation denotes those atoms related by the center of inversion. A projection of the $Cr(CO)_3$ onto the pyrene plane in Figure 4 shows a rotation angle of 12.8(7)° from an eclipsed position. The chromium is shifted from the ring center toward the outside of the ring by 0.03 Å. The pyrene ligand is planar to within 0.01 Å, and the bond length pattern is similar to that observed in the free ligand,[27,28] with a relatively short bond occurring between C(9) and C(10). As expected, the average aromatic ring C–C distance is slightly longer than the free ligand owing to the effects of complexation. Bond distances and angles for the asymmetric unit of the structure are shown in Tables VII and VIII, respectively.

**Table VII. Interatomic Distances (Å) for $(Cr(CO)_3)_2(pyr)$ (2)**

| | | | |
|---|---|---|---|
| Cr(1)–C(13) | 1.836(2) | C(10b)–C(10b)′ | 1.439(3) |
| Cr(1)–C(12) | 1.840(2) | C(3a)–C(3) | 1.417(2) |
| Cr(1)–C(11) | 1.852(2) | C(3a)–C(9)′ | 1.451(2) |
| Cr(1)–C(2) | 2.219(2) | C(3)–C(2) | 1.408(3) |
| Cr(1)–C(3) | 2.231(2) | C(2)–C(1) | 1.404(3) |
| Cr(1)–C(1) | 2.234(2) | C(1)–C(10a) | 1.420(2) |
| Cr(1)–C(3a) | 2.255(2) | C(10a)–C(10) | 1.457(2) |
| Cr(1)–C(10a) | 2.258(2) | C(10)–C(9) | 1.342(3) |
| Cr(1)–C(10b) | 2.271(2) | C(11)–O(11) | 1.133(3) |
| C(10b)–C(10a) | 1.422(2) | C(12)–O(12) | 1.151(2) |
| C(10b)–C(3a) | 1.432(2) | C(13)–O(13) | 1.162(2) |

**Table VIII. Bond Angles (deg) for $(Cr(CO)_3)_2(pyr)$ (2)**

| | | | |
|---|---|---|---|
| C(13)–Cr(1)–C(12) | 86.82(8) | C(1)–C(2)–C(3) | 121.00(16) |
| C(13)–Cr(1)–C(11) | 88.70(8) | C(2)–C(1)–C(10a) | 119.99(16) |
| C(12)–Cr(1)–C(11) | 89.71(9) | C(1)–C(10a)–C(10b) | 119.47(15) |
| C(10a)–C(10b)–C(3a) | 120.28(15) | C(1)–C(10a)–C(10) | 121.81(16) |
| C(10a)–C(10b)–C(10b)′ | 120.04(18) | C(10b)–C(10a)–C(10) | 118.72(15) |
| C(3a)–C(10b)–C(10b)′ | 119.67(18) | C(9)–C(10)–C(10a) | 121.32(16) |
| C(3)–C(3a)–C(10b) | 119.12(16) | C(10)–C(9)–C(3a)′ | 121.58(16) |
| C(3)–C(3a)–C(4) | 122.24(16) | O(11)–C(11)–Cr(1) | 177.68(19) |
| C(10b)–C(3a)–C(4) | 118.64(15) | O(12)–C(12)–Cr(1) | 177.95(18) |
| C(2)–C(3)–C(3a) | 120.14(17) | O(13)–C(13)–Cr(1) | 178.08(17) |

Both the solution and CP/MAS solid $^{13}C$ NMR spectra of **1** and **2** were determined. When the actual rotamer conformation for the $Cr(CO)_3$ moieties in **1** and **2** was known, a means of determining this conformation from NMR was sought. A broad featureless peak ($W_{1/2}$ = 3 ppm) was observed for the carbonyl absorption in the solid spectrum of **1**. Thus, even though **1** has six magnetically nonequivalent carbonyl groups, they could not be distinguished due to lack of resolution in the solid spectrum. In the solid NMR spectrum of **2** three absorptions could be seen at δ 227.6, 230.4, and 232.4 ppm with intensities in the approximate ratio of 3:6:10, respectively. Since three types of carbonyl groups are present in **2**, the number of peaks seems correct but they should appear in a 1:1:1 ratio. While accurate integration was not possible (due to noise) from the spectrum of **2**, the ratio was not 1:1:1. From these results it appears higher field and better signal to noise CP/MAS solid spectra will be necessary to establish the conformation of the $Cr(CO)_3$ rotamers by NMR.

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**Supplementary Material Available:** Tables of hydrogen coordinates, anisotropic thermal parameters and least squares planes for 1 and 2 (13 pages). Ordering information is given on any current masthead page.

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